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# JOURNAL

OF

# THE CHEMICAL SOCIETY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

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## General and Physical Chemistry.

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**A Unit for the Measurement of Light.** By W. SIEMENS (*Ann. Phys. Chem.*, **22**, 304).—The recent Conference at Paris for the determination of the units of electric quantities, adopted for their unit of light that which is given from a surface of fused platinum one centimetre square at the moment of its solidification (this vol., p. 2). The author has arranged an apparatus to realise this unit. The contrivance consists of a piece of very thin platinum foil, heated to its melting point by an electric current, while the light from it is allowed to pass through an aperture one-tenth of a square centimetre in area. This light is about equal of 1.5 English standard candles.

R. R.

**Specific Refractive Energy.** By J. KANNONIKOFF (*Bull. Soc. Chim.*, **41**, 548).—The author has determined the indices of refraction of the elements in the first two groups of the periodic system. These are calculated from the specific refractive energy of the corresponding salts of the organic acids, the specific refractive energy of the elements composing the latter being known. In taking the index of refraction for a ray of infinite wave-length, and grouping the elements according to the periodic law, perfect regularity is observed in the change of values.

<i>Group I.</i>		<i>Group II.</i>	
R <sub>A</sub> .	R <sub>A</sub> .	R <sub>A</sub> .	R <sub>A</sub> .
K = 7.51	Li = 2.97	Ca = 9.11	Mg = 6.57
Rb = 11.60	Na = 4.03	Sr = 11.23	Zn = 9.38
Cs = 18.84	Cu = 11.25	Ba = 15.40	Cd = 12.64
	Ag = 12.62		Hg = 19.40

The indices of refraction of the groups  $\text{NO}_3$  and  $\text{SO}_4$  (contained in nitrates and sulphates) were determined by subtracting the indices of the refraction of the metal from that of the sulphate or nitrate. In this way the author obtained the following mean values:  $\text{NO}_3 - R_A = 13.75$  and  $\text{SO}_4 - R_A = 16.80$ . These values enable him to form some conclusions as to the structure of nitric and sulphuric acids. Thus he

considers the structural formula of nitric acid to be  $\text{HO}-\text{N} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$  with triad nitrogen, and of sulphuric acid,  $\begin{array}{c} \text{HO} \\ \text{HO} \end{array} > \text{S} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$ , with hexad sulphur.

A. B.

**Electrical and Optical Units** (*Ann. Phys. Chem.* [2], 22, 616).—The following definitions were accepted by the International Conference which met at Paris, April 28th to May 3rd, 1884.

The *Ohm* is the resistance of a column of mercury of 0.01 square cm. section, and 106 cm. in length at a temperature of  $0^\circ \text{C}$ .

The *Ampère* is the current whose strength is equal to 0.1 C.G.S. electromagnetic units.

The *Volt* is the electromotive force which causes a current of an ampère in a conductor whose resistance is an ohm.

The *Unit of Homogeneous Light* is the quantity of light of that colour emitted in a normal direction from a square centimetre of the surface of molten platinum at the point of solidification.

The practical *Unit of White Light* is the quantity of light given off from the above illuminating source in the same direction.

V. H. V.

**A Constant Element for Electrical Measurements.** By W. v. BEETZ (*Ann. Phys. Chem.*, 22, 402—410).—The author has contrived a small dry Daniell cell, made of a glass tube, one half of which is filled by a plug made with dry gypsum mixed with concentrated solution of zinc sulphate, and the other half with the plaster similarly prepared with copper sulphate. In the former a copper, and in the latter a zinc, wire is fixed. The arrangement is very constant, its electromotive force showing little diminution for many hours, and being moreover but little affected by change of temperature.

R. R.

**Electricity of Flames.** By J. KOLLERT (*Ann. Phys. Chem.*, 22, 456—459).—This is a rejoinder to Elster and Geitel's paper in the controversy on this subject (*Abstr.*, 1884, p. 1238).

R. R.

**Electricity developed in the Disengagement of Gases.** By W. HANKEL (*Ann. Phys. Chem.*, 22, 387—402).—When a strip of platinum with earth connection was allowed to dip into water in a funnel, and the water as it slowly dropped from the drawn-out tube of the funnel was collected in a platinum basin, that water was found to have a charge of negative electricity. With a strip of copper, instead of platinum, the same result was obtained, but the charge was much weaker. Zinc, on the contrary, gave the water a positive charge. When the arrangement of the experiment was changed so that the metal instead of dipping into the funnel, received the drops of water therefrom,

as a strip inclined to the horizon, like results were obtained. When instead of water, acids of various kinds and strengths were allowed to drop on the strips of metal, and collected below in a platinum dish which, as also the strip of metal, could by means of a commutator be at will thrown into connection with the earth or with the electrometer gold-leaves, the charges of electricity were in general found liable to vary both in nature and quantity even with the same liquid and the same metal. Many circumstances are mentioned in the paper as affecting the results, such as the way in which the drops fall from the lower end of the strip, the adherence of froth thereto, &c. In the action of acids on metals, the containing vessels sometimes showed charges of one or other electricity; alternating several times in the course of a few minutes.

R. R.

**Depolarisation of an Electric Cell by Bromine.** By J. H. KOOSSEN (*Ann. Phys. Chem.* [2], 22, 348—350).—The depolarisation of the negative pole in an electric cell, by the direct combination of the hydrogen evolved with oxygen produced by the decomposition of higher oxides or their derivatives, suggested the use of bromine as one of the elements of a constant galvanic cell of strong electromotive force. The cell thus constructed consists of a glass vessel, narrowed at the lower extremity, into which is poured the bromine; on this rests a plate of clay, on which is placed a clay cell containing the amalgamed zinc cylinder. A platinum wire passes through the clay plate into the bromine. To complete the cell, the upper part of the apparatus is filled with dilute sulphuric acid, covered by a thin layer of petroleum to prevent the diffusion of the bromine into the atmosphere. The electromotive force of the combination, zinc, dilute sulphuric acid, bromine solution, platinum, is 1.9 volt; by substituting carbon for platinum, this value is increased. Its internal resistance is, however, greater than that of Grove's or Bunsen's cell, but notwithstanding in cases of large external resistance this cell presents the advantage of remaining constant for several months.

V. H. V.

**Apparatus for Breaking Electric Circuit in an Atmosphere of Hydrogen.** By C. L. R. E. MENGES (*Ann. Phys. Chem.* [2], 22, 156—157).—The apparatus described consists of a glass bulb blown out of a test-tube, into which are fused the platinum wires. The bulb previous to sealing is half filled with mercury, and the superincumbent layer of air displaced by hydrogen. Of the two wires one passes directly into the mercury, while the end of the other is immediately above its surface, so that by a slight rotation of the bulb it is also made to dip into the mercury. Thus the current can be completed or broken at will.

V. H. V.

**Electrical Conductivity of Acids.** By W. OSTWALD (*J. pr. Chem.*, 30, 93—95).—According to Faraday's law every electrolytic atom transfers an equal quantity of electricity, hence the electrical conductivity, with an equal number of electrolysable molecules, depends on the rapidity of the transference of the "ions." This again, according to Clausius' theory of electrolysis, is materially

influenced by the facility with which the electrolytes interchange their "zones." The rate of chemical reactions is further dependent on this facility. In his contributions to chemical dynamics, the author has shown that the rates of chemical reactions produced by acids are proportional to one another, in such a manner as to appear to be dependent upon a special property of each acid, which the author styles their affinity. Hence it appears probable that the rates of chemical action of acids and their electrical conductivities are proportional. This conclusion is satisfactorily supported by the results in the following table. The numbers in column I represent the electrical conductivities of different acids, that of hydrochloric acid taken as 100; those in columns II and III the affinities of these acids, as measured by their influence in producing methyl acetate and their inversion of cane-sugar respectively:—

	I.	II.	III.
Hydrochloric acid .....	100.0	100.0	100.0
Hydrobromic acid .....	101.0	98.0	111.0
Nitric acid .....	99.6	92.0	100.0
Ethylsulphonic acid ....	79.9	98.0	91.0
Isethionic acid.....	77.8	98.0	92.0
Phenylsulphonic acid....	74.8	99.0	104.0
Sulphuric acid.....	65.1	73.9	73.2
Formic acid .....	1.68	1.31	1.53
Acetic acid .....	0.424	0.345	0.4
Monochloracetic acid ....	4.9	4.3	4.84
Dichloracetic acid .....	25.3	23.0	27.1
Trichloracetic acid .....	62.3	68.2	75.4
Glycollic acid .....	1.34	—	1.31
Methylglycollic acid ....	1.76	—	1.82
Ethylglycollic acid.....	1.3	—	1.37
Diglycollic acid .....	2.58	—	2.67
Propionic acid.....	0.325	0.304	—
Lactic acid .....	1.04	0.9	1.07
$\beta$ -Hydroxypropionic acid.	0.606	—	0.808
Glyceric acid .....	1.57	—	1.72
Pyroracemic acid.....	5.6	6.7	6.49
Butyric acid.....	0.316	0.3	—
Isobutyric acid.....	0.311	0.268	0.335
Hydroxyisobutyric acid..	1.24	0.92	1.06
Oxalic acid .....	19.7	17.6	18.6
Malonic acid.....	3.1	2.87	3.08
Succinic acid .....	0.581	0.50	0.55
Malic acid.....	1.34	1.18	1.27
Tartaric acid .....	2.28	2.3	—
Racemic acid .....	2.63	2.3	—
Pyrotartaric acid.....	1.08	—	1.07
Citric acid .....	1.66	1.63	1.73
Phosphoric acid .....	7.27	—	6.21
Arsenic acid.....	5.38	—	4.81

P. P. B.

**Electromagnetic Rotation of the Plane of Polarisation of Light by Iron, Nickel, and Cobalt.** By A. KUNDT (*Ann. Phys. Chem.* [2], 23, 228—252).—Kerr has observed that the plane of polarisation of light, reflected normally from the polished pole of an electromagnet, is rotated (*Phil. Mag.* [5], 3, 321, and 5, 161—177). In this paper, these observations are confirmed, and it is further shown that transparent layers of iron, nickel, and cobalt in the magnetic field turn the plane of polarisation of the transmitted light most markedly. This rotation is for iron, for the rays of mean wave-length, about 30,000 greater than that of glass of equal thickness. In all cases the rotation is in the direction of the current of magnetisation, *i.e.*, in the positive direction. Kerr's observations regarding the reflection from polished electromagnetised steel are extended to those of nickel and cobalt, and it is shown that in transmission, as also in reflection, the rotation-dispersion is anomalous, *i.e.*, the red rays are rotated more than the blue. Complicated phenomena are observed by the oblique reflection from the polar or side surfaces, but may be explained on the supposition that the light, in the course of reflection, passes through a thin layer of the metal, wherein it undergoes a negative rotation.

V. H. V.

**A Freezing Apparatus.** By E. LOMMEL (*Ann. Phys. Chem.* [2], 23, 614—616).—In this paper, an apparatus is described for effecting the solidification of water by means of a reduction of pressure by an air-pump, and condensation of the water-vapour evolved by concentrated sulphuric acid.

V. H. V.

**Thermal Conductivity of Tourmaline.** By F. STENGER (*Ann. Phys. Chem.* [2], 22, 522—528).—S. P. Thompson and Lodge have observed (*Phil. Mag.* [5], 8, 18) an unilateral conductivity for heat in the direction of the principal axis, and further that the coefficient of conductivity from the antilogous towards the analogous pole differs from the conductivity in the reverse direction, their ratio being as the numbers 100 : 119. Their observations were not, however, sufficiently numerous, nor is there any degree of certainty whether the crystals used for experiment were homogeneous. In this paper, an account is given of experiments conducted with two perfectly homogeneous specimens of crystals from Brazil and Ceylon. The apparatus used was that proposed by Weber, which consists of a copper cylinder, connected on its upper service with a thermopile and galvanometer, and on to its lower surface the crystal under examination is fastened by solder. The lower surface of the crystal is brought into contact with a plate of ice by means of a suitable arrangement, and observations are made by the galvanometer of the changes of temperature. The antilogous and analogous pole were placed alternately on the copper cylinder, but the curves, of which the abscissæ represent the time in seconds from the first contact with the ice, and the ordinates the corresponding temperatures, were found to be practically identical. This result proves that the unilateral conductivity is either practically inconsiderable, or in all probability has no existence.

V. H. V.

**Absorption of Heat by Water-vapour.** By W. C. RÖNTGEN (*Ann. Phys. Chem.* [2], 23, 1—49, and 259—298).—The absorption

of heat by water-vapour, strenuously maintained by Tyndall (*Phil. Trans.*, 1882), and denied by Magnus, involves a point of considerable meteorological importance. In these papers, an elaborate account is given of experiments on this question, based on the following principle: if a gas be contained in a vessel, whose walls are more or less diathermic, and heated by an external source of radiation, its rise of temperature will be dependent mainly on two conditions, firstly, on the heat obtained indirectly from the warm sides of the vessel, and secondly, on the heat absorbed by the gas itself. Under the same conditions the former is independent of the nature of the gas, while the latter is variable according to the degree of absorption of thermic rays by the gas. If then two gases be submitted in succession to the same source of radiation, and it be found that the temperature of the one reaches a higher point after the interval of a given time than the other, it is to be concluded that the former is the greater absorbent of heat rays. The apparatus used consisted mainly of a thick walled, gilded brass tube, one side of which was closed by a plate of rock-salt, the other by a gilded brass plate. The rays passing through the former were reflected by the latter, and thus the maximum absorption was obtained. This absorption tube was connected with the form of manometer known as Marey's drum, which consists essentially of a membrane of caoutchouc drawn over a metallic case, and connected with which is a delicate needle, registering its movements on a rotating cylinder. By these means the most minute variations of pressure could be graphically represented. With this apparatus, the degree of absorption of heat was determined of hydrogen, damp air, and air containing the normal atmospheric proportion of carbonic anhydride. From the principle enunciated above, it is obvious that the increase of pressure occasioned by the rise of temperature is separable into two parts, *i.e.*, permanent increase caused by the warming of the walls of the vessel, and temporary increase caused by the absorption of heat rays by the gas. Experiments showed that the former was constant for the same source of radiation, for damp or dry air, or pure hydrogen, but the latter for dry air, saturated with moisture at  $0^{\circ}$ , and heated to  $26^{\circ}$ , was equal to 2.18 mm., a Bunsen burner being used as a source of radiation; water-vapour is thus an absorbent of the ultra-red or thermic rays. The amount of absorption effected by air containing the normal proportion of carbonic anhydride was, however, exceedingly small. Experiments were also made to determine the degree of absorption of the solar rays, and of rays from terrestrial sources by the environing atmosphere, but the places selected, Giessen and Pontresina, were situated at presumably insufficient altitudes to give satisfactory results. Other experiments are also described in detail, in which the oxyhydrogen flame, or flasks filled with boiling water or boiling aniline were used as sources of radiation, or in which plates of other material were substituted for the rock salt; these all tended to confirm the result described above. V. H. V.

**New Method of Determining Specific Heats.** By J. THOULET and H. LAGARDE (*Jahrb. f. Min.*, 1884, 2, Ref., 297—298).—The authors have devised a method of determining specific heats, which

requires at most 0.5 gram of the substance, allows more than 10 determinations in an hour, and renders all calculations for corrections unnecessary. As calorimeter, two glass cylinders are employed, each with  $\frac{1}{2}$  to  $\frac{2}{3}$  c.c. water. In one of these vessels, the substance is placed in grains, after having been warmed in a glass tube in the mouth to about  $36^{\circ}$ . The increase of temperature it effects in the water (of about  $24^{\circ}$ ) can be measured to  $0.01^{\circ}$  by means of two thermopiles connected together through the bottoms of the two vessels and a Weber galvanometer. As a standard, copper is employed, the specific heat of which ( $c_1$ ) was found by Regnault to be 0.09515. The specific heat of the substance ( $c$ ) may, provided that equal weights of copper and of the substance are employed, be found from the equation—

$$c_1 = \frac{c \cdot P \cdot C_1 \cdot d_1}{p \cdot c \cdot (d - d_1) + P \cdot C \cdot d},$$

in which  $P$  is the weight of the calorimetric liquid,  $C$  its specific heat,  $p$  the weight of the substance,  $d$  and  $d_1$  the deflection of the galvanometer by the substance and the copper respectively.

In order to be able to dip into the water, immediately after the substance, the copper, which has been simultaneously warmed in a second glass tube placed in the mouth, recourse is had to a third glass cylinder, also provided with a thermopile. In order to obtain accurate results, care must be taken that the magnetic needle stands exactly at zero. At the commencement of the experiment, the liquids in the glass cylinders must be brought to the same temperature by means of the galvanometer (zero). The substance and the copper must not be heated to too great an extent, and but little substance and liquid must be employed, so that the temperature in the calorimeter may become constant as soon as possible. Loss of heat by radiation is almost entirely avoided, from the rapidity of the process, if each calorimetric vessel is surrounded by a second larger cylinder, the lid of which closes the inner vessel at the same time. B. H. B.

### Specific Heat of Gaseous Elements at High Temperatures.

By BERTHELOT and VIEILLE (*Bull. Soc. Chim.*, **41**, 561—566).—The authors have continued the observations of Vieille (*Abstr.*, 1883, 771, 898), and find in accordance with Mallard and Le Chatelier (*Abstr.*, 1883, 542, 844) that the specific heats of nitrogen, hydrogen, oxygen, and carbonic oxide are nearly the same at all temperatures. From their observations on gaseous explosive mixtures (*Abstr.*, 1884, 709, 804), they calculate that the mean specific molecular heat of each gas at constant volume between 0 and  $t$  is  $6.7 + 0.0016 (t - 2800)$ , where  $t$  is from  $2800^{\circ}$  to  $4400^{\circ}$ . From  $0^{\circ}$  to  $200^{\circ}$  the specific molecular heats of these gases are about 4.8. They are therefore doubled in the rise of temperature from  $0^{\circ}$  to  $4500^{\circ}$ . The specific molecular heat of chlorine appears by some observations both at low and high temperature to be greater. A. B.

**Specific Heat of Steam and Carbonic Anhydride at High Pressure.** By BERTHELOT and VIEILLE (*Bull. Soc. Chim.*, **41**, 566—

570).—The specific molecular heat of steam at constant volume between 0 and  $t$  calculated by the authors from their previous observations may be expressed by the formula  $16.2 + 0.0019 (t - 2000)$  when  $t$  is from 2000 to 4300, and that of carbonic anhydride  $19.1 + 0.0015 (t - 2000)$ . Both gases appear, therefore, to have at a high temperature greater specific heats than at the ordinary temperatures. A. B.

**Influence of Concentration on the Specific Heat of Aqueous and Alcoholic Solutions of Metallic Chlorides.** By A. BLÜMCKE (*Ann. Chim. Phys.* [2], **23**, 161—173).—Former researches have established that the specific heat of aqueous solutions of salts decrease with increase of concentration, but no general law has been deduced from which the specific heat of such solutions can be calculated from that of their constituents. In this paper, experimental values are given for the specific heat of aqueous solutions of sodium, barium, mercuric and manganous chlorides, and of alcoholic solutions of zinc, ferric, mercuric, manganous, zinc and ferric chlorides. The results adduced confirm the above generalisation. A comparison of the observed specific heat for unit mass with the specific heat calculated on the supposition that the dissolved salt is not chemically combined with the solvent, shows great irregularities in either direction; these are undoubtedly due to a difference in condition of the undissolved and dissolved salt, arising probably from a more intimate association of the salt with the molecule of the solvent, such as might lead to the production of a hydrate or alcoholate respectively.

In a note, the author adds a determination of the specific heat of metallic uranium made with the improved Bunsen ice calorimeter used for the above experiments, the mean value was  $\cdot 0280$  (comp. Abstr., 1881, 1031). V. H. V.

**Heat of Combination of Hydrogen with Oxygen.** By A. BOILLOT (*Compt. rend.*, **99**, 712—714).—Two-thirds of the heat of formation of water is developed by the hydrogen and one-third by the oxygen, this being the proportion by volume in which the gases combine. The water formed absorbs no latent heat, and in the formation of 18 grams of water the 2 grams of hydrogen develop 46 cal. and the 16 grams of oxygen 23 cal. Hydrogen peroxide contains the two gases in equal volumes, and in the formation of this compound each constituent develops the same amount of heat, viz., 23.7 cal. for 34 grams of peroxide. The latent heat of this quantity of peroxide is 44.6 cal., one-half of which is proper to each constituent.

The considerations on which these conclusions are based also show that the sp. gr. of liquid oxygen is  $\frac{8}{9}$  or 0.888. Wroblewski found 0.89—0.90. C. H. B.

**Heat of Formation of some Soluble Compounds and the Law of Thermal Substitution Constants.** By D. TOMMASI (*Bull. Soc. Chim.*, **41**, 532—541).—The author gives a large number of instances in which the heats of formation of soluble compounds are found by the experiments of others to agree with those calculated by



the law of thermal substitution constants, and shows that in the cases of sodium sulphite and hydrogen sodium sulphite, the numbers lately found by De Forcrand (Abstr., 1884, 803) agree with those previously calculated. The differences between the estimated and calculated heats of formation of certain copper, lead, and mercury salts, which have been brought forward by Berthelot (Abstr., 1884, 702), as instances of the inaccuracy of the law may, according to the author, be due to dissociation, or may disappear with more careful observation.

A. B.

**Relation between the Density and Viscosity of Liquids.** By L. WARBURG and J. SACHS (*Ann. Phys. Chem.* [2], 22, 518—522).—The earlier experiments of Coulomb established that the friction of water was independent of the pressure, a result corroborated by the researches of Poiseuille. Warburg and Babo have however shown that the viscosity of liquid carbonic anhydride at 25.1° is increased in the ratio 628:800 by a rise of pressure from 70 to 105 atmospheres. But this change is probably dependent on the variation of density accompanying that of pressure. Then, if in other liquids the change in viscosity is in the same direction as that of liquid carbonic anhydride, it is evident that no variation will be observable within narrow, but only within wide variations of pressure, *i.e.*, from 1 to 100—150 atmospheres. By means of a suitable apparatus it was ascertained that the viscosity of liquid carbonic anhydride, ether, and benzene, increases with increase of pressure, whilst that of water decreases.

V. H. V.

**Apparatus for the Determination of Vapour-densities at Low Temperatures.** By N. v. KLOBUKOFF (*Ann. Phys. Chem.* [2] 22, 465—492). The principle of the apparatus described in this paper is that of the so-called weight-thermometer. It consists essentially of a cylindrical glass vessel filled with mercury, into which by suitable means is introduced a small glass bottle containing a weighed quantity of the liquid whose vapour-density it is desired to determine. If the weight of the mercury contained originally in the vessel be known, and also the weight expelled at the given temperature of the experiment, then from the weight of mercury (in excess of the latter quantity) expelled by the vaporisation of the liquid and of the mercury remaining in the vessel, the volume occupied by the weighed quantity of the liquid can be determined. This apparatus, it is proposed to call the "Vapour-density Dilatometer." The experimental results obtained with liquids of various boiling points are adduced, and the observed values for the vapour-densities approximate very closely to those required by theory.

V. H. V.

**Estimation of Vapour-densities of Liquids of High Boiling Point.** By N. v. KLOBUKOFF (*Ann. Phys. Chem.* [2], 22, 493—509).—The apparatus described is based on the principle of the hydrometer, and consists of a small cylindrical glass vessel, provided with an arrangement at its summit for bearing weights; at the lower end is an aperture for communication of the liquid contained in the hydro-

meter with that in which it floats, and for introducing within a glass bottle the liquid whose vapour-density is required. If then in a blank experiment, the hydrometer sinks to a certain mark, and there be introduced the liquid, which is converted into a state of vapour, a portion of the liquid contained in the hydrometer is forced out, whereby the hydrometer becomes lighter and rises. Weights must then be added to restore it to its original position. In the experiments detailed, the hydrometer was filled with and floated in mercury, and from the quantity of mercury forced out by the vaporisation of the liquid, as indicated by the difference in weights required for the immersion of the hydrometer to the given mark, the volume occupied by the weighed quantity of the liquid can be determined. It is proposed to call this apparatus the "Vapour-density Areometer." Experiments with chloroform, ethyl alcohol, and benzene, are quoted, and the results were satisfactory even with small quantities of these liquids. It is proposed to carry on investigations on the vapour-densities of iodine and sulphur with a modified form of this apparatus.

V. H. V.

**Diffusion of Gases and Vapours.** By A. WINKELMANN (*Ann. Phys. Chem.*, **22**, 152—161).—In this, his second paper on the subject (*ibid.*, **22**, 1), the author adduces experiments and discussions to show how the determination of the coefficients of diffusion of vapours through gases is affected by the nature of the gas, the velocity of saturation, and other circumstances. His final and corrected values for the combinations experimented on are as follows—water-vapour into hydrogen at 49·5° being taken as unity—

	49·5°.	92·4°.
Water-vapour into hydrogen .....	1·0000	1·1794
"    "    air .....	0·2827	0·3451
"    "    carbonic anhydride ..	0·1811	0·2384

R. R.

**Diffusion of Homologous Ethereal Salts.** By A. WINKELMANN (*Ann. Chim. Phys.* [2], **23**, 203—227).—The rates of transpiration of homologous ethereal salts and their coefficient of friction have been the subject of various investigations by Meyer and Schumann (*Abstr.*, 1881, 504), Puluje, and others. In this paper, an account is given of experiments made with a view of determining the diffusion coefficient of ethereal salts, and of the molecular path-length of their vapours deduced therefrom. Air, hydrogen, and carbonic anhydride were chosen as the media into which the vapours diffused, and their coefficients for normal pressure and experimental temperature,  $\tau$ , were calculated according to the formula

$$K = \frac{(h + h_0)(h_1 - h_0)}{2} \cdot \frac{S}{d_1} \cdot \frac{273 + \tau}{273} \cdot \frac{1}{(t_1 - t_2) \{ \log_n P - \log_n (P - p) \}}$$

in which  $h_1$  and  $h_0$  are the lengths in mm. of the liquid vaporised,

S the density of the liquid at temperature  $\tau$ ,  $d$  the density of its vapour,  $P$  the atmospheric pressure, and  $p$  the pressure of the saturated vapour at  $\tau$  (about  $72^\circ$ ). In the series of tables are given the experimental values for the various ethereal salts, and the results so obtained are reduced to normal pressure and temperature on the hypothesis that the diffusion coefficient decreases in proportion to the square of the absolute temperature.

The following table contains some of these reduced results, the upper number giving the result for air, the middle for hydrogen, and the lower for carbonic anhydride:—

TABLE I.

	Diffusion coefficients at $0^\circ$ and 760 mm.				
	Methyl.	Ethyl.	Propyl.	Isobutyl.	Amyl.
Formate .....	—	$\left\{ \begin{array}{l} 0\cdot0863 \\ 0\cdot3349 \\ 0\cdot0566 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0739 \\ 0\cdot2888 \\ 0\cdot0503 \end{array} \right\}$	—	—
Acetate .....	$\left\{ \begin{array}{l} 0\cdot0877 \\ 0\cdot3401 \\ 0\cdot0588 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0709 \\ 0\cdot2727 \\ 0\cdot0487 \end{array} \right\}$	—	$\left\{ \begin{array}{l} 0\cdot0533 \\ 0\cdot2224 \\ 0\cdot0397 \end{array} \right\}$	—
Propionate .....	$\left\{ \begin{array}{l} 0\cdot0750 \\ 0\cdot2952 \\ 0\cdot0528 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0644 \\ 0\cdot2460 \\ 0\cdot0445 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0554 \\ 0\cdot2121 \\ 0\cdot0396 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0506 \\ 0\cdot1998 \\ 0\cdot0365 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0442 \\ 0\cdot1796 \\ 0\cdot0319 \end{array} \right\}$
Butyrate.....	$\left\{ \begin{array}{l} 0\cdot0644 \\ 0\cdot2435 \\ 0\cdot0425 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0566 \\ 0\cdot2232 \\ 0\cdot0400 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0523 \\ 0\cdot2059 \\ 0\cdot0364 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0474 \\ 0\cdot1850 \\ 0\cdot0332 \end{array} \right\}$	—
Isobutyrate.....	$\left\{ \begin{array}{l} 0\cdot0644 \\ 0\cdot2610 \\ 0\cdot0452 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0569 \\ 0\cdot2293 \\ 0\cdot0409 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0539 \\ 0\cdot2120 \\ 0\cdot0388 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0468 \\ 0\cdot1889 \\ 0\cdot0336 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0426 \\ 0\cdot1724 \\ 0\cdot0305 \end{array} \right\}$
Valerate .....	—	$\left\{ \begin{array}{l} 0\cdot0505 \\ 0\cdot2050 \\ 0\cdot0366 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0466 \\ 0\cdot1891 \\ 0\cdot0341 \end{array} \right\}$	$\left\{ \begin{array}{l} 0\cdot0423 \\ 0\cdot1694 \\ 0\cdot0308 \end{array} \right\}$	—

It will be seen from the above table (I) that the diffusion coefficients of isomeric salts are approximately equal, and (II) that they decrease slightly with increase of molecular weight. But if the air diffusion coefficients be multiplied by the densities of their vapours the values so obtained are approximately equal, varying from  $0\cdot216$  to  $0\cdot243$ , so that in such a homologous series the following result obtains. "*Under the same conditions of temperature and pressure equal masses of the various vapours diffuse in equal time.*" But these generalisations do not hold good for vapours of all liquids of analogous molecular constitution, as those of water, alcohol, and ether. From the results

in the above table, the mean path-length of the molecule can be deduced from Stefan's formula—

$$k = \frac{3\pi\sqrt{2}}{8} \cdot \omega \cdot \sqrt{m} \cdot \sqrt{\frac{m_1 + m_2}{m_1 m_2}} \cdot \left( \frac{1}{\sqrt{l_1}} + \frac{1}{\sqrt{l_2}} \right)^2,$$

adopting for the mean path-length of the mixed molecules of air, of hydrogen, and carbonic anhydride respectively, the calculated values of Obermayer (comp. *Wien. Ber.*, **73**, 1876).

The following table contains the mean values for the path-lengths of the molecules of the vapours of the above ethereal salts.

TABLE II.

*Mean Path-lengths*  $\times 10^8$  *in centimetres at 0° and 760 mm.*

$C_3H_6O_2$ .....	220.5	$C_7H_{14}O_2$ .....	119.0
$C_4H_8O_2$ .....	181.0	$C_8H_{16}O_2$ .....	105.0
$C_5H_{10}O_2$ .....	152.5	$C_9H_{18}O_2$ .....	94.8
$C_6H_{12}O_2$ .....	133.0		

The mean path-length thus decreases with increase of molecular weight. The diameter of the sphere of the molecule is inversely proportional to its path-length, and its volume inversely proportional to the third power of the square root of its path-length; below are given the value for  $\frac{1}{l}10^{-4}$  and  $\left(\frac{1}{l}\right)^{\frac{3}{2}}10^{-7}$  for the above ethereal salts.

	$\frac{1}{l}10^{-4}$ .	$\left(\frac{1}{l}\right)^{\frac{3}{2}}10^{-7}$ .
$C_3H_6O_2$ .....	45.3	30.5
$C_4H_8O_2$ .....	55.3	43.5
$C_5H_{10}O_2$ .....	65.4	56.4
$C_6H_{12}O_2$ .....	75.4	69.4
$C_7H_{14}O_2$ .....	85.4	82.3
$C_8H_{16}O_2$ .....	95.4	95.3
$C_9H_{18}O_2$ .....	105.5	108.3

It is thus seen that for every addition of  $CH_2$  to the molecule the diameter of the molecular sphere and also its volume increase by a constant quantity. But it is to be observed that the volume of the molecule is only inversely proportional to the value  $\frac{1}{l^{\frac{3}{2}}}$ , provided that the arrangement of the atoms within the molecule is of the same kind, *i.e.*, that the molecule is of the same linear extension in every direction. The regularity of increase of the volume with increase of molecular weight affords a confirmation of this view, *i.e.*, of a flat tessellated arrangement of the atoms within the molecule, and excludes the hypothesis of a spherical arrangement. V. H. V.

**Saline Solutions.** By C. BENDER (*Ann. Phys. Chem.*, **22**, 179—203).—In general the liquid produced by the mixture of solutions of

two salts having no chemical action on each other, or by the mixture of a stronger and a weaker solution of the same salt, has physical constants not agreeing with those which are the arithmetical mean calculated from the constituent solutions. Nevertheless, it is possible, as the author's researches show, so to adjust the proportions of the saline constituents that admixtures shall have constants agreeing with the calculated mean value. Such solutions are termed by him "corresponding solutions." The results given in the paper go to prove that in these "corresponding solutions" the numbers of molecules of the salt contained in equal volumes have a simple ratio to each other. The constants discussed in the paper relate to density, tension, and electric conductivity.

R. R.

**An Elementary Demonstration of Avogadro's Law.** By G. KREBS (*Ann. Phys. Chem.*, **22**, 295—303).

**The Periodic Law and the Occurrence of the Elements in Nature.** By T. CARNELLEY (*Ber.*, **17**, 2287—2291).—From a consideration of the periodic system of the elements, the author is led to the following conclusions. The terms *even* and *uneven* series refer to the arrangement of the elements in Mendelejeff's table of the periodic law.

I. Elements which belong to *uneven* series are generally easily reducible, those belonging to *even* series reducible with difficulty.

II. Elements belonging to *uneven* series seldom occur in a free state in nature, those belonging to *even* series often do so occur.

III. Elements belonging to *uneven* series occur generally as sulphides or double sulphides (*i.e.*, in combination with a negative element belonging to an *uneven* series) and seldom as oxides, those belonging to *even* series generally occur as oxides (carbonate, sulphates, &c.), *i.e.*, in combination with a negative element belonging to an *even* series.

With reference to Lothar Meyer's curve ("Moderne chemische Theorieen") these conclusions may be expressed as follows:—

Elements which occur on a *falling* part of the curve are reducible with difficulty, and very seldom found in nature in the free state or as sulphides, but always in combination with oxygen; whereas elements which occur on a *rising* part of the curve are easily reducible, and are almost always found in nature in the free state or as sulphides, and very seldom as oxides.

L. T. T.

**New Apparatus for Laboratory Use.** (*Dingl. polyt. J.*, **254**, 67—79).—This paper contains short descriptions of new apparatus, illustrated with woodcuts, and comprises the following: Sample-taker for chemical products, H. Angerstein; parting funnel, Currier; funnel to cover evaporating vessels, V. Meyer; temperature regulator, V. Meyer; pressure regulator for fractional distillation under reduced pressures, L. Godefroy; fractional distillation for the valuation of chemical products, G. Lunge, also the Commission of Verein für Chemische Industrie; polarising apparatus, F. Schmidt and Hansch; titrating apparatus for beet-root juice, G. Hoppe; titrating apparatus,

E. Greiner ; pipette-burette, R. Hübner ; cylinder-burette, T. Pusch ; apparatus for the estimation of the hardness of water, G. Loges ; decomposing flask for Scheibler's carbonic acid apparatus, G. Loges ; apparatus for the estimation of carbon in iron and steel, N. B. Wood, also A. B. Clemence ; apparatus for the decomposition of ores by means of chlorine, R. Schelle ; lamp for burning petroleum of low boiling point, C. Lilienfein ; spirit-lamp, C. Reinhardt. J. T.

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## Inorganic Chemistry.

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**Dispersion-equivalent of the Diamond.** By A. SCHRAUF (*Ann. Phys. Chem.*, **22**, 424—429).—The dispersion-equivalent of a Brazilian diamond, determined by the author, was 0.03286. He discusses the extreme smallness of this number as compared with the same constant in some series of organic bodies, which show an increase of its value with increase of the proportion of carbon.

R. R.

**Liquid Carbonic Oxide.** By V. OLSZEWSKI (*Compt. rend.*, **99**, 706—707).—Carbonic oxide carefully purified from carbonic anhydride forms a transparent colourless liquid under pressure between  $-139.5^{\circ}$  and  $-190^{\circ}$ , but in a vacuum it solidifies at  $-211^{\circ}$  to a snow-like mass, if the pressure has been reduced rapidly, but to a compact opaque mass if the pressure has been reduced slowly. If the pressure is reduced so gradually that the liquefied gas does not boil but evaporates only from the surface, the liquid forms a transparent solid. When the pressure rises to one atmosphere the solid melts to a colourless liquid. The following table shows the relation between the pressure and the boiling point of liquid carbonic oxide:—

Pressure in atmos.	Temp.	Pressure in atmos.	Temp.
35.5	— $139.5^{\circ}$ (critical point)	16.1	— $154.4^{\circ}$
25.7	— $145.3$	14.8	— $155.7$
23.4	— $147.7$	6.3	— $168.2$
21.5	— $148.8$	4.6	— $172.6$
20.4	— $150.0$	1.0	— $190.0$
18.1	— $152.0$	Vacuum	— $211.0$ (solidifies)

Although, in the gaseous state, carbonic oxide resembles nitrogen in many of its properties, the two substances behave somewhat differently at very low temperatures. The critical point of carbonic oxide, and its boiling point under atmospheric pressure, are several degrees higher than those of nitrogen. Carbonic oxide solidifies in a vacuum, but a low temperature alone is not sufficient to solidify nitrogen. Moreover, the temperature obtained by the evaporation of liquid carbonic oxide in a vacuum is higher than that obtained by the evaporation of liquid nitrogen under the same conditions. The differences

are doubtless due to the presence of a solid element in the carbonic oxide.  
C. H. B.

**Phosphorus Trifluoride.** By H. MOISSAN (*Compt. rend.*, 99, 655—657).—Phosphorus trifluoride is obtained by heating carefully dried copper phosphide with lead fluoride free from silica, in a brass tube, and drying the product over pumice moistened with sulphuric acid. It is a colourless gas which does not liquefy under a pressure of 180 atmos. at 24°, but under a pressure of 40 atmos. at -10° forms a colourless very mobile liquid, which does not attack glass. The sp. gr. of the gas is 3.022 (calculated 3.0775).

Phosphorus trifluoride is incombustible when mixed with air, but explodes when it is mixed with half its volume of oxygen and brought in contact with a flame or electric spark. When pure, it does not fume in the air, but it is decomposed slowly in presence of water at the ordinary temperature, with formation of hydrofluoric and phosphorous acids,  $\text{PF}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HF}$ . When mixed with steam at 100°, the decomposition of the fluoride is much more rapid. Solutions of sodium or potassium hydroxide rapidly absorb the trifluoride, with elevation of temperature and formation of a fluoride and a phosphite. Solutions of barium hydroxide or potassium carbonate absorb the gas more slowly. Phosphorus trifluoride is immediately decomposed by solutions of chromic acid or potassium permanganate, and is instantly absorbed by bromine. It is also absorbed by alcohol with development of heat, and is not given off again when the liquid is boiled. When passed over boron or silicon at a dull red heat, it yields boron or silicon fluoride, and it is rapidly decomposed by melted sodium, more slowly by heated copper. It combines with ammonia gas, forming a very light, woolly, white compound, which is decomposed by water.

When mixed with half its volume of oxygen and subjected to the action of an electric spark, phosphorus trifluoride explodes violently, and the compound formed fumes in the air and is instantly absorbed by water with formation of phosphoric acid, but no trace of phosphorous acid. The gas thus produced seemed to be phosphorus oxyfluoride,  $\text{PF}_3\text{O}$ .

When heated in contact with glass, phosphorus trifluoride is decomposed with separation of phosphorus and formation of silicon fluoride, and the volume of the silicon fluoride thus formed furnishes a means of estimating the amount of fluorine in the phosphorus fluoride.  
C. H. B.

**Phosphorus Chloronitride.** By A. W. HOFMANN (*Ber.*, 17, 1909—1912).—The formula for this body has long been established as  $\text{P}_3\text{N}_3\text{Cl}_6$ , but little work has been done on the subject. The author has made experiments to determine whether the chlorine-atoms can be replaced by other radicals.

Aniline dissolves this chloronitride to a clear solution, which, however, soon solidifies to a crystalline mass. The principal products are a crystalline substance, very sparingly soluble in alcohol, and an amorphous compound, easily soluble. The crystalline substance is best purified by solution in glacial acid. It yields well-formed needles

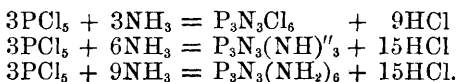


melting at  $268^{\circ}$ , and has the formula  $P_3N_3(NHPh)_6$ . Its formation would be expressed by the equation—



Paratoluidine yields a similar crystalline compound, melting at  $243^{\circ}$ . Piperidine acts strongly with the chloronitride, producing piperidine chloride and an amorphous substance, easily soluble in alcohol, insoluble in water.

The author is inclined to look upon the group  $P_3N_3$  as playing an important part, and to consider that the formula of phospham should be trebled, and would then become  $P_3N_3(NH)''_3$ . This would be analogous to an aniline compound,  $P_3N_3(NPh)''_3$ . The substance,  $P_4N_3(NHPh)$ , described above gives off aniline when heated, and leaves a resinous mass, which may contain the compound,  $P_3N_3(NPh)''_3$ . It is also probable that other ammonio-derivatives might be prepared somewhat according to the following equations:—



L. T. T.

**Action of Nitric Acid on Tellurium.** By D. KLEIN and J. MOREL (*Compt. rend.*, **99**, 540—542).—Pulverulent tellurium, obtained by precipitation with sulphurous acid, dissolves readily in dilute nitric acid, with evolution of nitrogen oxides. The temperature at which solution takes place is lower the higher the concentration of the acid; with acid of sp. gr. 1.25 the action begins at  $-11^{\circ}$ . At a low temperature solution is not complete, and a greyish curdy residue is left, which afterwards turns white, and forms long flexible microscopic needles containing both nitric and telluric acid. The solution, when diluted with water, deposits "tellurous hydrate" or tellurous anhydride, a certain quantity of basic tellurium nitrate (*Abstr.*, 1884, p. 1256) always remaining in solution. "Tellurous hydrate" is formed when the nitric acid is dilute (sp. gr. 1.1—1.2) and the action takes place at a low temperature. It is a white curdy substance which gradually changes to a yellowish-white mass of microscopic rectangular lamellæ of tellurous anhydride; these act strongly on polarised light. When the reaction takes place at a higher temperature, or if stronger nitric acid is used, tellurous anhydride is formed in microscopic quadratic octahedra. The nitric acid solution spontaneously deposits octahedral crystals of tellurous anhydride, and if the nitric acid employed is somewhat dilute (sp. gr. about 1.2), and the temperature has not risen above  $30^{\circ}$  during the reaction, the precipitation of tellurous anhydride is accelerated by heat. Under these conditions, about half the tellurium remains in solution in the form of nitrate, which crystallises out when the liquid is concentrated and cooled. When the octahedral crystals of tellurous anhydride are boiled with nitric acid of sp. gr. 1.35, they yield a solution of the basic nitrate.

Tellurous anhydride requires 150,000 parts of water for solution.

C. H. B.

**Action of Water and Nitric Acid on Basic Tellurium Nitrate.** By D. KLEIN and J. MOREL (*Compt. rend.*, **99**, 567—569).

—Basic tellurium nitrate (Abstr., 1884, 1256) is slowly decomposed by water in the cold, nitric acid and a very small quantity of tellurous anhydride being dissolved, whilst tellurous anhydride is left undissolved in rectangular lamellæ. At a higher temperature, decomposition is almost instantaneous; the solution becomes strongly acid, and the greater part of the tellurous anhydride remains undissolved in the form of microscopic octahedra. These facts explain the commonly accepted statement that tellurous anhydride is slightly soluble in water, but does not redden blue litmus. Tellurous nitrate does not act on moistened litmus in the cold until after several hours, and when decomposition takes place the solution of a small quantity of tellurous anhydride is due to the presence of the free nitric acid.

Basic tellurium nitrate dissolves in nitric acid and crystallises readily when the solution is concentrated and cooled. It seems to be much more soluble in the dilute than in the concentrated acid. Solutions in nitric acid of sp. gr. 1.1—1.4 are stable at all temperatures, and solutions in acid of sp. gr. about 1.35, are not decomposed on addition of 100 vols. of water. On the other hand, solutions in nitric acid of sp. gr. 1.1 are decomposed by water with precipitation of tellurous anhydride, decomposition being more rapid the greater the proportion of water. The limit of decomposition appears to be reached when the solution is mixed with 5 vols. of water; under these conditions, the precipitation of tellurous anhydride is very slow, and with a smaller proportion of water no decomposition takes place. The tellurous anhydride deposited when the nitric acid solutions are diluted, does not crystallise in octahedra, but in some perfectly distinct form.

Basic tellurium sulphate,  $(\text{TeO}_2)_2\text{SO}_3$ , decomposes in a similar manner. C. H. B.

**Preparation of Potassium Chlorate.** By E. K. MUSPRATT and G. ESCHHELLMANN (*Dingl. polyt. J.*, **254**, 90).—Chlorine is passed into magnesia mixed with water, and the solution is evaporated to 35—50° B., so that, on cooling, some magnesium chloride crystallises out. The product is now treated with potassium chloride, when potassium chlorate and magnesium chloride are formed; the greater portion of the former may then be obtained by crystallisation. The mother-liquor, which retains 5—10 per cent. of the total potassium chlorate, is treated with hydrochloric acid and steam, by which potassium chloride is formed and chlorine is evolved; the latter may be absorbed by lime or magnesia. The solution containing an excess of acid is now neutralised with magnesium carbonate, and a solution of magnesium chloride containing potassium chloride is formed. This is evaporated to 45° B., and allowed to cool, when it sets. In this state, it may go into commerce, or magnesia may be obtained from it by heating, and this can again be employed in the process. J. T.

**Preparation of Sodium Chlorate.** By E. K. MUSPRATT and G. ESCHHELLMANN (*Dingl. polyt. J.*, **254**, 47).—Chlorine is passed to

saturation into water holding magnesia in suspension, so that one equivalent of magnesium chlorate to  $5-5\frac{1}{2}$  equivalents of chloride go into solution. This solution can be concentrated by evaporation to  $35-40^{\circ}\text{B.}$ , so that on cooling a part of the chloride crystallises out. The solution, now containing four equivalents of chloride to one of chlorate, or the original solution if preferred, is treated with sodium hydroxide or carbonate, or a mixture of the two. Magnesia, magnesium carbonate, or a mixture of the two, as the case may be, is precipitated whilst sodium chloride and chlorate remain in solution. On concentrating by evaporation to  $48-50^{\circ}\text{B.}$ , and cooling, the chlorate separates out. The magnesia residue is employed again directly, or if it contains carbonate, after being calcined. J. T.

**Crystallised Argentammonium Chloride and Bromide.** By TERREIL (*Bull. Soc. Chim.*, **41**, 597).—Argentammonium chloride and bromide were obtained in a crystalline form by heating the dry salts, saturated with ammonia gas, with a strong aqueous solution of ammonia in sealed tubes. The method, as well as the properties of the crystals, have been described in a former Abstract (Abstr., 1884, 890).

W. R. D.

*Note by Abstractor.*—The author states that the argentammonium chloride and bromide have never before been crystallised. This, however, is incorrect. Faraday, in 1818 (*Journ. Science and Arts*, **5**, 74), obtained a crystalline argentammonium chloride by dissolving silver chloride in strong solution of ammonia and allowing the liquid to stand. Transparent crystals  $\frac{1}{4}$ -inch wide were deposited in flat rhombohedra, in some of which two acute angles were missing, which caused them to appear like hemihedra. The crystals lost ammonia and became opaque when exposed to air, and were similarly decomposed by water with separation of silver chloride. An argentammonium bromide having analogous properties, was prepared in the same way by Liebig (*Schweig. Journ.*, **48**, 103).—W. R. D.

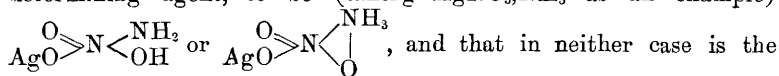
**Argentammonium Phosphate.** By O. WIDMANN (*Ber.*, **17**, 2284—2285).—With reference to Reychler's communication on this subject (Abstr., 1884, 1261), the author states that in 1874 he described (*Oefvers. of Kongl. Vet. Akad. Förhandlingar*, Stockholm, 1874, No. 4, p. 41), a crystalline diammonio-silver phosphate,  $\text{Ag}_3\text{PO}_4\cdot 4\text{NH}_3$ . It was obtained by evaporating an ammoniacal solution of silver phosphate in a desiccator over quicklime with which a little ammonium chloride had been mixed. It formed colourless prismatic needles resembling the arsenate. The probable constitution is  $\text{AgO}\cdot\text{PO}(\text{ONH}_3\cdot\text{NH}_3\text{Ag})_2$ . The crystals turn yellow on exposure to the air, and give up all their ammonia over sulphuric acid. With ammonia and dry silver phosphate, the author obtained results similar to Reychler's.

L. T. T.

**Argentammonium Compounds.** By A. REYCHLER (*Ber.*, **17**, 2263—2266).—Ammonia is rapidly absorbed by silver citrate with considerable development of heat and a discoloration of the salt: about 4—5 mols.  $\text{NH}_3$  are thus absorbed. Silver citrate dissolves

readily in ammonia, and alcohol precipitates from this solution *hex-ammonio-silver citrate* as a thick syrup, easily soluble in water. Silver benzoate absorbs dry ammonia to form *diammonio-silver benzoate*, a white substance insoluble in water. Carey-Lea has described (*Chem. News*, 1861) a yellow crystalline diammonio-silver picrate. The power of the picrate to absorb ammonia is probably due to its nitro-groups. Ammonium picrate absorbs 1 mol.  $\text{NH}_3$  at  $0^\circ$  to form *mon-ammonio-ammonium picrate*,  $\text{C}_6\text{H}_2(\text{NO}_3)_3 \cdot \text{ONH}_4 \cdot \text{NH}_3$ : at summer heat (about  $26^\circ$ ) scarcely a trace of ammonia is absorbed.

The author considers the constitution of the diammonio-compounds of the organic acids to be probably  $\text{R}-\text{OAg} > \text{C} < \begin{smallmatrix} \text{ONH}_2 \\ \text{NH}_2 \end{smallmatrix}$ , and of the mono-ammonio-compounds, where he considers the nitro-group to be the determining agent, to be (taking  $\text{AgNO}_3 \cdot \text{NH}_3$  as an example)



ammonia united to the silver.

L. T. T.

**Preparation of Strontium and Barium Chlorides.** By WACKENRODER (*Dingl. polyt. J.*, 253, 440).—The author proposes to add to a solution of strontium or barium sulphide an equivalent amount of calcium chloride, and pass carbonic anhydride into the mixture. Hydrogen sulphide is disengaged and a solution of strontium or barium chloride obtained, whilst calcium carbonate is precipitated; the latter is removed by filtration, and the solution evaporated and allowed to crystallise.

D. B.

**Constitution of Bleaching Powder.** By E. DREYFUS (*Bull. Soc. Chim.*, 41, 600—609).—The formula proposed by Stahlschmidt ( $2\text{CaHClO}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$ ) alone accounts for the excess of calcium hydroxide that is invariably present in this compound. Assuming this formula, bleaching powder should contain 39.01 per cent. of available chlorine, but experiment shows that it often contains more than 40 per cent., which appears to militate against the assumption. But the use of moist lime in the manufacturing process explains this result. The water acts on the bleaching compound  $\text{CaHClO}_2$ , producing calcium hypochlorite, together with free calcium hydroxide,  $2\text{CaHClO}_2 = \text{Ca}(\text{OH})_2 + \text{Ca}(\text{ClO})_2$ . The calcium hydroxide then again combines with chlorine. According to this, the active compound in bleaching powder is  $\text{CaHClO}_2$  with more or less calcium hypochlorite. Stahlschmidt's formula also supposes the existence of calcium chloride in bleaching powder. This has been considered to be incorrect, as bleaching powder is said not to yield calcium chloride when treated with alcohol. The author disputes this assertion, and states that calcium chloride is always dissolved from the compound by alcohol, in quantity which increases with the time during which the alcohol is in contact. Lunge and Schäppi (Abstr., 1880, 789), arguing from the action of carbonic anhydride on bleaching powder, whereby nearly the whole of the chlorine is evolved, have also arrived at the conclusion that calcium chloride is not a constituent of bleaching

powder. The author points out that this conclusion is erroneous; for although carbonic anhydride does not act on calcium chloride alone, yet in presence of hypochlorous anhydride (from the action of carbonic anhydride on  $\text{CaHClO}_2$ ), the following reaction occurs either with dry calcium chloride or with its aqueous solution:  $\text{CaCl}_2 + \text{CO}_2 + \text{Cl}_2\text{O} = \text{CaCO}_3 + 2\text{Cl}_2$ . In order to determine that the calcium hydroxide precipitated by water from bleaching powder is an essential constituent, the following experiments were made:—Solid bleaching powder was treated with ammonia and alcohol; the liquid was boiled, filtered, diluted with water, and the calcium estimated as oxalate. In another experiment, dry bleaching powder was melted at a red heat to expel oxygen and chlorine; the residue, treated with alcohol and water, was filtered, and the calcium estimated in the filtrate as oxalate. The results of these two experiments, which determine the amount of calcium as chloride, were identical. It is further shown that with two carefully prepared specimens of bleaching powder, the calcium obtained as chloride by the ammonia method is just half of the total calcium combined with available chlorine, the other half having been precipitated as hydroxide. This is in accordance with the following equations:— $2[2(\text{CaHClO}_2) + \text{CaCl}_2] + 2\text{NH}_4\text{OH} = 2\text{NH}_4\text{Cl} + 3\text{CaCl}_2 + 3\text{Ca}(\text{OH})_2 + 2\text{O}_2$ , and at a red heat  $2[2(\text{CaHClO}_2) + \text{CaCl}_2] + \text{H}_2\text{O} = 3\text{CaCl}_2 + 3\text{Ca}(\text{OH})_2 + \text{Cl}_2 + 3\text{O}$ . The author concludes, therefore, that the formula of bleaching powder should be written  $2\text{CaHClO}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$ .

W. R. D.

**Peroxides of the Zinc-magnesium Group.** By R. HAASS (*Ber.*, 17, 2249—2255).—Thénard (*Ann. Chim. Phys.*, 1818, 9, 55, and *Mém. de l'Acad. des Sciences*, 3, 429) described the formation of a "deutoxide de zinc" by (A) solution of zinc hydroxide in a hydrochloric solution of hydroxyl, and reprecipitation with potash or soda, and (B) by acting directly on gelatinous zinc hydroxide with hydroxyl. On estimating the excess of oxygen in his compounds, Thénard found that the additional oxygen taken up was rather more than half that originally present in the monoxide; and concluded from this that the peroxidation was incomplete. These results appear to have been very generally overlooked, or when noticed (as in Gmelin-Kraut's Handbook), mistrusted. The author has therefore repeated Thénard's experiments and fully confirms his results.

The author employed the methods used by Thénard, but modified (A) so far as to mix a solution of a pure zinc salt with an aqueous solution of hydroxyl, and then precipitate with ammonia. The author was not able to obtain the pure peroxide, the precipitate always containing unoxidised zinc hydroxide. The composition of the precipitate dried at  $110^\circ$ , varied between  $\text{Zn}_3\text{O}_8$  and  $\text{Zn}_3\text{O}_5$ . By numerous modifications of the mode of preparation, the author endeavoured to obtain the peroxide free from the hydroxide, but in every case where the precipitation of hydroxide was avoided, no formation of peroxide took place, so that the author is inclined to consider the presence of hydroxide as essential to such formation.

As rightly described by Thénard, zinc peroxide (or rather its mixture with the monoxide) is a white, odourless, tasteless, and neutral

gelatinous mass. This substance is tolerably stable towards water, acids, and heat. A sample which had been heated at  $120^{\circ}$  for 12 hours, and subsequently more strongly heated in a test-tube, still gave the hydroxyl reaction very strongly when dissolved in hydrochloric acid. The author has also obtained similar results with cadmium, the compounds obtained varying between  $\text{Cd}_5\text{O}_8$  and  $\text{Cd}_3\text{O}_5$ . Manganese, which in other ways may be easily converted into the dioxide, yielded by the above treatment results almost exactly agreeing with those obtained with zinc and cadmium. The composition of the precipitates varied between  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_5$ . Magnesium appears to form a similar peroxide, but with more difficulty, the highest stage of oxidation yet obtained being expressed by  $\text{MgO} : \text{Op} = 93 : 7$ , where Op represents the additional oxygen. Up to the present, no evidence of the existence of a peroxide of beryllium could be obtained.

L. T. T.

**Decomposition of Cupric Oxide by Heat.** By DEBRAY and JOANNIS (*Compt. rend.*, **99**, 533—587).—It is well known that cupric oxide is decomposed when strongly heated, and it is generally believed that the product of decomposition is an oxide,  $\text{Cu}_2\text{O}_3$ , or  $\text{Cu}_5\text{O}_4$ , intermediate between cuprous and cupric oxides.

If cupric oxide yields the oxide  $\text{Cu}_5\text{O}_4$  when heated, it ought to have a constant tension of dissociation until one-fifth of the oxygen has been expelled, at which point the tension will change to that of the intermediate oxide; but if, on the other hand, the cupric oxide is decomposed simply into cuprous oxide and oxygen, and the so-called intermediate oxide is really a *mixture* of these two bodies, the tension of dissociation of the cupric oxide should remain constant until half the oxygen is expelled, at which point it will change to that of the cuprous oxide.

Direct experiments show that when cupric oxide is heated in a vacuum, it begins to decompose at a dull red heat, and if the temperature is so regulated that the oxide does not fuse, the tension of dissociation of the latter remains constant until very nearly half of the oxygen is expelled. If the apparatus is allowed to cool, any oxygen remaining within it is *completely* absorbed by the cuprous oxide, and when the residue is cold, it is found to consist of cuprous oxide in those parts which have been most strongly heated, and of cupric oxide in those parts which have been somewhat cooler, the line of separation of the two oxides being perfectly sharp and distinct. The same results are obtained with various samples of cupric oxide previously partially decomposed by fusion. It follows, therefore, that when cupric oxide is heated under these conditions, it is decomposed into oxygen and cuprous oxide only, without forming any intermediate oxide.

If the cupric oxide is heated to fusion, it is decomposed somewhat rapidly, but the tension of dissociation varies with the state of decomposition of the oxide, and diminishes rapidly as the residue becomes more completely converted into cuprous oxide. When the partially decomposed oxide is allowed to cool slowly in the apparatus, the pressure of the oxygen diminishes until the moment of solidification, when it suddenly increases, quickly attains a maximum, and then, as

cooling continues, diminishes again, finally becoming *nil* if the absorbing surface is sufficiently large. These phenomena are easily explained if it is admitted that the dissolution of a dissociable body in a liquid incapable of combining with it lowers the tension of dissociation of that body in the same way as the vapour-tensions of liquids are modified when certain liquids are mixed. On this assumption, the tension of dissociation of cupric oxide, fused with an increasing proportion of cuprous oxide, diminishes as the proportion of cuprous oxide increases; but when the residue solidifies and forms a mixture of the two oxides which do not act on one another, the cupric oxide regains its original properties, and more especially its true tension of dissociation, hence the sudden increase of pressure at this point.

C. H. B.

**Oxidation of Copper.** By DEBRAY and JOANNIS (*Compt. rend.*, 99, 688—692).—When copper is heated in presence of air, it is converted into cupric oxide without intermediate formation of cuprous oxide, at all temperatures between that at which oxidation begins (about  $350^{\circ}$ ), and that at which the tension of dissociation of the oxide formed amounts to one-fifth of the atmospheric pressure, *i.e.*, the pressure of the oxygen in the air. Beyond this temperature, the cupric oxide at first formed is partially decomposed, and when the mixture of cuprous and cupric oxide melts, decomposition ceases as soon as the variable and diminishing tension of the oxygen in the mixture amounts to one-fifth of the atmospheric pressure. The composition of the mixture will depend on the temperature. A similar result is obtained by direct oxidation of copper at these high temperatures; a fused product is always obtained consisting of a mixture of cuprous and cupric oxides, in proportions varying with the temperature.

If the partially decomposed oxide is allowed to cool in the air, it is completely reoxidised if sufficiently porous; but if it has been fused, oxidation takes place only on the surface, and the solidified residue has practically the same composition as the liquid. It is evident that in determinations of copper as cupric oxide the temperature must not be sufficient to melt the oxide.

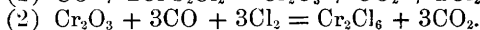
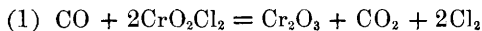
When the copper is present in large excess, the product of oxidation is cupric oxide alone, if the temperature is below redness; but if the temperature is sufficiently high to partially dissociate the cupric oxide, the latter is decomposed into cuprous oxide and oxygen, and the oxygen thus given off at once combines with the excess of copper, forming a further quantity of cuprous oxide. A mixture of cupric oxide and metallic copper cannot in fact exist at a temperature at which the oxide begins to dissociate, for the oxygen given off is at once absorbed by the metallic copper, and thus is prevented from acquiring a tension sufficiently high to arrest decomposition.

In cases where the amount of oxygen is not sufficient to oxidise the copper completely, but is more than sufficient to convert it into cuprous oxide, the product is a mixture of the cuprous and cupric oxides (preceding Abstract). Cuprous oxide absorbs oxygen even more readily than metallic copper; hence if the preceding mixture is allowed to cool in air or in oxygen, the cuprous oxide is completely

oxidised. The readiness and completeness with which cuprous oxide absorbs oxygen when moderately heated may be used as a means of obtaining a very perfect vacuum.

C. H. B.

**Some Reactions of Chromyl Dichloride.** By QUANTIN (*Compt. rend.*, **99**, 707—709).—Chromic chloride,  $\text{Cr}_2\text{Cl}_6$ , can be prepared by passing a mixture of chlorine and carbonic oxide over chromium sesquioxide, heated to redness; and is readily obtained in violet crystals by passing vapour of chromyl dichloride, chlorine, and carbonic oxide through a glass tube heated at  $500\text{--}600^\circ$ ;  $2\text{CrO}_2\text{Cl}_2 + 4\text{CO} + \text{Cl}_2 = 4\text{CO}_2 + \text{Cr}_2\text{Cl}_6$ . In this reaction, the chromyl dichloride is not first reduced to chromous chloride by the carbonic oxide, for if a mixture of chromyl dichloride with carbonic oxide alone is passed through the hot tube, vivid combustion takes place with formation of green chromium sesquioxide and violet chromic chloride. The progress of the first reaction may be represented by the following equations:—



The carbonic oxide combines only with the oxygen which would have been liberated by the action of heat alone, and does not reduce the sesquioxide which is formed, but the latter is converted into chromyl dichloride by the action of the chlorine which is liberated and the excess of carbonic oxide. The same results are obtained with any mixture which will give off chromyl dichloride. Dry hydrochloric acid gas acts slightly on chromyl dichloride at a red heat, a certain quantity of chlorine, water-vapour, and black chromium oxide being formed, but no violet oxychloride is produced. When chromyl dichloride is decomposed by heat, the only products are chlorine, oxygen, and black chromium oxide.

C. H. B.

**Chromammonium Compounds. Luteochromium Salts.** By S. M. JØRGENSEN (*J. pr. Chem.*, **30**, 1—32).—In a former communication (this Journal, Abstr., 1882, 1167), the author pointed out that a solution of chromammonium chloride in ammoniac chloride undergoes oxidation in absence of air, heat is produced and hydrogen evolved, and the chief product is the roseo-chloride. If the mixture is cooled and the oxidation takes place slowly, then luteochromium chloride is the chief product. To prepare this compound, a solution of chromous chloride, prepared by Christensen's method, is forced by hydrogen pressure into a vessel containing a mixture of 700 grams of ammonium chloride and 750 c.c. solution of ammonia (sp. gr. 0.91). The vessel, entirely filled with this mixture, is closed by a stopper, through which passes a delivery tube opening under water. The vessel is surrounded by cold water to moderate the reaction. The evolution of hydrogen takes place slowly and ceases in about 24 hours, the undissolved ammonium chloride is covered with the luteochromium chloride, a portion of which is also contained in the solution, from which it may be obtained by precipitation with alcohol; the precipitate after being washed with alcohol is dried, dissolved in warm water, and the solution filtered into nitric acid (sp. gr. 1.39); in this manner a precipitate



of luteochromium nitrate is obtained. The nitrate is washed with dilute nitric acid (1 vol. of nitric acid to 2 vols. of water), and the acid removed by washing with dilute alcohol.

The luteochromium chloride mixed with the ammonium chloride is separated by repeated treatment with water, the aqueous extracts are precipitated by nitric acid, and thus further quantities of luteochromium nitrate are obtained.

Blomstrand's method of preparing luteocobalt salts may be applied for the preparation of luteochromium salts.

*Luteochromium nitrate*,  $\text{Cr}_212\text{NH}_3, 6\text{NO}_3$ , is obtained from dilute solutions on addition of concentrated nitric acid in long narrow prisms; from concentrated solutions, dilute nitric acid precipitates it in orange-yellow, lustrous, quadratic tables. It may be crystallised from warm water containing nitric acid, and then forms small quadratic pyramids.

*Luteochromium nitrate sulphate*,  $\text{Cr}_212\text{NH}_3, 2\text{NO}_3, 2\text{SO}_4$ , obtained by adding dilute sulphuric acid to a solution of the nitrate, or by addition of ammonium sulphate and ammonia, forms yellow, lustrous, quadratic octahedra.

*Luteochromium nitrate platinochloride*,  $\text{Cr}_212\text{NH}_3, 2\text{NO}_3, 2\text{PtCl}_6 + 2\text{H}_2\text{O}$ , an orange-yellow crystalline precipitate, formed when hydrogen platinochloride is added to a solution of the luteo-nitrate.

*Luteochromium chloride*,  $\text{Cr}_212\text{NH}_3, \text{Cl}_6 + 2\text{H}_2\text{O}$ , is best obtained by first treating a saturated solution of the nitrate with concentrated hydrochloric acid and mercuric chloride, a yellow precipitate of the compound  $\text{Cr}_212\text{NH}_3, \text{Cl}_6, 2\text{HgCl}_2$  is obtained. This mercury compound suspended in water, and decomposed by sulphuretted hydrogen, gives a solution from which, on evaporation, the luteochromium chloride separates in large yellow crystals. It is converted by concentrated hydrochloric acid into the chloropurpureo-chloride.

*Luteochromium platinochlorides*; three such compounds have been obtained: (a)  $\text{Cr}_212\text{NH}_3, 3\text{PtCl}_6 + 6\text{H}_2\text{O}$  is formed as an orange-yellow crystalline precipitate when sodium platinochloride is added to a dilute solution of the neutral luteo-chloride; (b)  $\text{Cr}_212\text{NH}_3, \text{Cl}_6, 2\text{PtCl}_6 + 5\text{H}_2\text{O}$  is produced when an acid solution of the luteo-chloride is precipitated by a solution of platinic chloride; it forms long orange-yellow needles; by cold water, it is resolved into luteo-chloride and the salt  $\alpha$ . When the salt (b) is washed with dilute hydrochloric acid, it is converted into the compound  $\text{Cr}_212\text{NH}_3, \text{Cl}_6, \text{PtCl}_6 + 2\text{H}_2\text{O}$ .

*Luteochromium bromide*,  $\text{Cr}_212\text{NH}_3, \text{Br}_6$ , prepared by the action of hydrobromic acid on a half-saturated solution of the nitrate; it forms an orange-yellow crystalline precipitate, and is less soluble than the chloride.

*Luteochromium platinobromide*,  $\text{Cr}_212\text{NH}_3, 3\text{PtBr}_6 + 4\text{H}_2\text{O}$ , prepared by adding a dilute solution of sodium platinobromide to a dilute solution of the luteo-bromide. It forms a precipitate consisting of deep vermillion, lustrous, quadratic, and eight-sided tables. When less dilute solutions are employed, or the above precipitate is allowed to stand, a change takes place, and a compound similar to the luteochromium platinochloride with  $6\text{H}_2\text{O}$  is formed.

*Luteochromium iodide*,  $\text{Cr}_212\text{NH}_3, \text{I}_6$ , is formed by treating a solution

of the nitrate with solid potassic iodide: the yellow precipitate is washed with hydriodic acid, dissolved in water, and filtered into hydriodic acid. It crystallises in lustrous rhombic tablets, and is isomorphous with the bromide.

*Luteochromium iodide sulphate*,  $\text{Cr}_212\text{NH}_3\text{I}_2\cdot 2\text{SO}_4$ , is formed by treating an ammoniacal solution of the chloride with ammonium iodide and ammonium sulphate. It crystallises in octahedra.

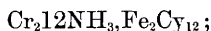
*Luteochromium sulphate*,  $\text{Cr}_212\text{NH}_3\cdot 3\text{SO}_4 + 5\text{H}_2\text{O}$ , is prepared by neutralising luteochromium hydroxide (formed by rubbing together the luteo-bromide and moist silver oxide) with sulphuric acid, and precipitating the solution with alcohol; it crystallises in long, yellow, lustrous crystals.

*Luteochromium sulphate platinochloride*,  $\text{Cr}_212\text{NH}_3\cdot 2\text{SO}_4\cdot \text{PtCl}_6$ , is obtained as an orange-yellow precipitate.

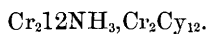
*Luteochromium orthophosphate*,  $\text{Cr}_212\text{NH}_3\cdot 2\text{PO}_4 + 8\text{H}_2\text{O}$ , obtained by treating a solution of the nitrate with sodium phosphate and ammonia, as a yellow precipitate consisting of yellow shining needle-shaped crystals.

*Luteochromium oxalate*,  $\text{Cr}_212\text{NH}_3\cdot 3\text{C}_2\text{O}_4 + 4\text{H}_2\text{O}$ , obtained as a crystalline precipitate by decomposing the nitrate with ammonium oxalate.

The following salts have been prepared in a similar manner: the *pyrophosphate*,  $\text{Cr}_212\text{NH}_3\cdot 2(\text{P}_2\text{O}_7\text{Na}) + 23\text{H}_2\text{O}$ ; the *ferricyanide*,



the *cobalticyanide*,  $\text{Cr}_212\text{NH}_3\cdot \text{Co}_2\text{Cy}_{12}$ ; and the *chromicyanide*,



P. P. B.

**Double Tungstates of Rare Metals.** By HÖGBOM (*Bull. Soc. Chim.*, **42**, 2—6).—By methods of fusion, a large number of compounds of sodium tungstate with the metals of the rare earths were obtained; these crystallised in the same form as the simple tungstates described by Cossa. The salts may be prepared by dissolving the oxides with tungstic acid, in fused sodium tungstate, or in fused sodium chloride, or still better in a fused mixture of the two. The mixture is liquefied at a bright red heat, and maintained in a semi-liquid condition at low redness. Microscopic crystals of the salts are formed and separated by treating the product with water, in which they are insoluble. Weak acids attack them only slowly in the cold, but they are completely decomposed by repeated treatment, in a finely powdered condition, with concentrated hydrochloric acid. It was in this way that the analyses of the greater number were made; the others were fused with a mixture of alkaline carbonates, and the tungstic acid precipitated by mercuric nitrate. Notwithstanding the difference in composition, the salts bear a great resemblance to one another in crystalline form, which is generally that of a tetragonal octahedron. These were not obtained large enough to measure the angles exactly, but an approximate measurement was made with the aid of the microscope. The salts described may be arranged under the following types:—

- I.  $\left\{ \begin{array}{c} 4\text{Na}_2\text{O} \\ \text{R}_2\text{O}_3 \end{array} \right\} 7\text{WO}_3$ ; R = La, Ce, or G.  
 II.  $\left\{ \begin{array}{c} 3\text{Na}_2\text{O} \\ \text{R}_2\text{O}_3 \end{array} \right\} 6\text{WO}_3$ ; R = Di.  
 III.  $\left\{ \begin{array}{c} 3\text{Na}_2\text{O} \\ 2\text{R}_2\text{O}_3 \end{array} \right\} 9\text{WO}_3$ ; R = La, Sm, Er.  
 IV.  $\left\{ \begin{array}{c} \text{Na}_2\text{O} \\ \text{R}_2\text{O}_3 \end{array} \right\} 4\text{WO}_3$ ; R = Di.  
 V.  $\left\{ \begin{array}{c} 2\text{Na}_2\text{O} \\ \text{RO}_2 \end{array} \right\} 4\text{WO}_3$ ; R = Th.

The salts of the types I, II, and V are formed in presence of excess of sodium tungstate, and those of the types III and IV in presence of excess of sodium chloride. In a note appended to this paper, Cleve comments on the remarkable fact of the similarity in crystalline form of these different salts, all of which either crystallise in the same form or in that of scheelite, which is isomorphous with fergusonite. Other cases of apparently anomalous isomorphism occur with the rare earths and oxides of the formula RO. Thus titanite is isomorphous with yttrtitanite, and according to Nordenskiöld, cerite,  $2\text{C}_2\text{O}_3, 3\text{SiO}_2$ , with peridote,  $2\text{MgO}, \text{SiO}_2$ . It would thus appear that isomorphism is possible between compounds of the rare earths and of the oxides of the form RO when the total proportion of oxygen is the same in the basic and acid oxides which constitute the compounds. The formulæ of the metallic oxides of the cerium and yttrium groups have been so firmly established in other ways, that it is undesirable to change them solely on account of the isomorphism of certain of their tungstates with scheelite.

W. R. D.

**The Tempering of Steel.** By C. FROMME (*Ann. Phys. Chem.*, 22, 371—387).—The changes of density and of hardness in iron or steel heated, and either slowly cooled or suddenly quenched in water, are the subjects investigated in the author's experiments. In tempered steel the density and hardness by no means go together, for increased density more often corresponds with diminished hardness and *vice versa*. The results recorded in the paper support the theory that in tempering there takes place not only the mechanical and purely physical process of sudden contraction, but also another process of a chemical nature consisting chiefly in the combination of the iron with the free carbon distributed through its mass.

R. R.

### Mineralogical Chemistry.

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**Effect of Heat on Vesuvian, Apatite, and Tourmaline.** By C. DOELTER (*Jahrb. f. Min.*, 1884, **2**, Mem., 217—221).—The author has elaborately investigated the effect of heat on the optical properties of vesuvian, apatite, and tourmaline. He finds that the optical pro-

properties of vesuvian are very variable, not only in crystals from different localities, but also in those from the same locality. Many vesuvians are quite normal and exhibit the black cross in all positions of the plate; this is the case with the light-green variety from Ala. Much more frequent is the case in which a distinct separation of the arms of the cross occurs. Crystals from Vesuvius present a small axial angle of  $4^{\circ}$  to  $8^{\circ}$ , and other crystals may be mentioned which exhibit a considerable axial angle. Thus, an axial angle of  $34\frac{1}{2}^{\circ}$  for red light was measured on a light-brown crystal from Vesuvius,  $24^{\circ}$  on a yellowish-brown crystal from Piedmont, and  $12^{\circ}$  on a brown crystal from Zermatt. The vesuvians differing optically also present differences on being heated. With the vesuvians which have a very small axial angle, this usually increases with increase of temperature, whilst with those which have a large axial angle, it decreases.

Apatite, according to Mallard, exhibits optical anomalies. This the author found to be the case with the violet apatites from Schlaggenwald and Ehrenfriedersdorf, and with coloured apatites generally; whilst the colourless crystals from Pfitsch, and the pale-green crystals from Salzbach, were perfectly normal. A yellowish-brown crystal of tourmaline from Lower Drauburg, in Carinthia, exhibited an axial angle of  $9^{\circ}$  for red light. With a slight increase of temperature, no change could be detected; and at a red heat the arms of the hyperbola came nearer together, but did not even at the highest temperature join completely.

B. H. B.

**Sulphur from Zielenzig.** By A. ARZRUNI (*Jahrb. f. Min.*, 1884, 2, Ref., 307).—Rhombic crystals of sulphur occur in fissures in the lignite at the Phoenix Mine, near Zielenzig, in Brandenburg. The crystals have been formed by sublimation. The following forms were observed: P, 0P,  $P\infty$ ,  $\infty P$ ,  $P\infty$ ,  $\frac{1}{2}P$ ,  $\frac{1}{3}P$ ,  $\frac{1}{6}P$ .

B. H. B.

**Minerals of the Cryolite-group from Greenland.** By A. KRENNER (*Jahrb. f. Min.*, 1884, 2, Ref., 308—310).—This paper contains an account of the morphological and optical properties of the cryolite minerals: cryolite, thomsenolite, pachnolite, arksutite, and ralstonite.

B. H. B.

**Microscopic Association of Magnetite with Titanite and Rutile.** By A. CATHREIN (*Jahrb. f. Min.*, 1884, 2, Ref., 306—307).—Magnetite surrounded by titanite, disseminated through a mixture of chlorite and actinolite, occurs in remarkably fine examples in rocks from the Alpbach and Wildschönau valleys in the Tyrol. A mixture of magnetite, with actinolite and a little titanite, was obtained after repeated washing and extraction with the magnet. This mixture, in very fine powder, after a quarter of an hour's treatment with hydrochloric acid, left a residue consisting of rutile and some actinolite. The latter was isolated and analysed (II). The acid solution exhibited the composition given under I, 0.3565 gram being employed, with 0.1215 insoluble residue containing 0.11  $\text{SiO}_2$ , 0.017  $\text{TiO}_2$ , and 0.093 pure actinolite—

	Calculated.				
	I.	Magnetite.	Titanite.	Actinolite.	II.
SiO <sub>2</sub> .....	4·67	—	1·63	3·04	55·38
TiO <sub>2</sub> .....	5·07	2·90	2·17	—	—
Al <sub>2</sub> O <sub>3</sub> ....	—	—	—	—	—
Cr <sub>2</sub> O <sub>3</sub> ....	3·65	3·65	—	—	0·50
Fe <sub>2</sub> O <sub>3</sub> ....	52·94	52·94	—	—	—
FeO.....	29·75	29·25	—	0·50	9·16
CaO ....	2·27	—	1·52	0·75	13·65
MgO ....	2·41	1·28	—	1·13	20·62
H <sub>2</sub> O.....	—	—	—	—	0·27
Total ..	100·76	90·02	5·32	5·42	99·58

The 90·02 per cent. of magnetite calculated to 100 gave the following results :—

TiO <sub>2</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	Total.
3·22	4·06	58·81	32·49	1·42	100·00

From the author's observations, it follows that the so-called leucoxene surrounding magnetite is a product of alteration. In the magnetite, Fe<sub>2</sub>O<sub>3</sub> is replaced by FeTiO<sub>3</sub>, and leucoxene, which is nothing other than titanite, is formed. The microscopic investigation supports this theory.

B. H. B.

**Pseudomorphs after Rutile.** By A. V. LASAULX (*Jahrb. f. Min.*, 1884, 2, Ref., 299).—Pseudomorphs after rutile occur in the granite of Morbihan. Rutile crystals are of frequent occurrence, but they are often altered to a considerable depth into ilmenite. Between the layer of ilmenite and the rutile, yellow titanite hydrate is frequently met with. In other crystals, a product resembling titanomorphite occurs in the immediate neighbourhood of the ilmenite. Other rutile crystals were altered into a mixture of ferric oxide, minute crystals of anatase, titanite, and rutile. In this case, the anatase is paramorphous after rutile.

B. H. B.

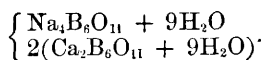
**Natural Borates.** By C. RAMMELSBURG (*Jahrb. f. Min.*, 1884, 2, Mem., 158—163).—On the banks of a salt lake in the Argentine province of Jujuy, Brackenbusch collected a white mud which hardened to a solid mass, on exposure to the atmosphere. This substance is boronatrocalcite (Dana's ulexite), and contains sodium chloride and a little clay. It is free from sulphates, but several of the harder particles appear to be glauberite. When heated, the powder fuses to a cloudy green glass. Analysis gave the following results :—

B <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
42·06	15·91	8·90	33·48	100·35

from which the author calculates the formula to be: Na<sub>4</sub>Ca<sub>4</sub>B<sub>18</sub>O<sub>33</sub> + 27H<sub>2</sub>O; this requires :—

B <sub>3</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
43·03	15·30	8·47	33·20	100·00

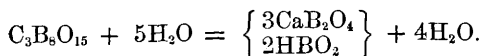
If the formula is written—



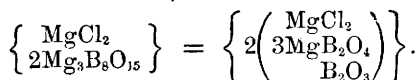
and if the borate  $\text{R}'\text{BO}_2 = \text{R}''\text{B}_2\text{O}_4$ , the oxygen ratio for bases and acid is 2 : 3.

In conclusion the author gives a summary of the natural borates, assuming that  $\text{R}'\text{BO}_2 = \text{R}''\text{B}_2\text{O}_4$ .

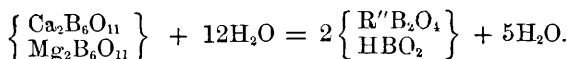
A. *Oxygen Ratio for Bases and Acid*, 3 : 4.—1. Priceite (a mineral from Oregon identical with pandermite from Panderma on the Black Sea)—



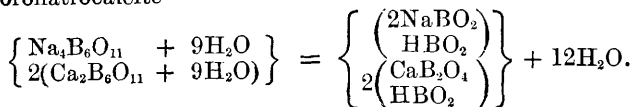
2. Boracite (and Stassfurtite)—



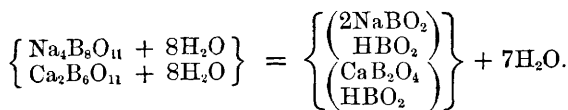
B. *Oxygen Ratio for Bases and Acid*, 2 : 3.—1. Hydroboracite.



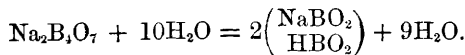
2. Boronatrocalcite—



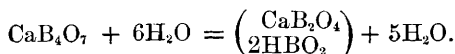
3. Franklandite (*Phil. Mag.*, 1877, 284)—



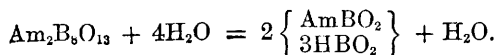
C. *Oxygen Ratio for Bases and Acid*, 1 : 2.—1. Borax (Tinkal);—



2. Borocalcite (Hayesine, Tiza of Atacama)—

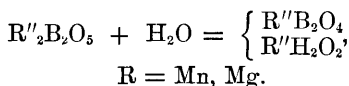


D. *Oxygen Ratio for Bases and Acid*, 1 : 4.—1. Larderellite.

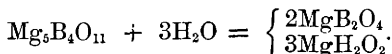


In addition to the above are two basic borates.

1. *Sussexite*—



2. *Spaibelyite*—



In *ludwigite*, *datolite*, *danburite*, *tourmaline*, and *axinite*, boron must be regarded as replacing Al or Fe. B. H. B.

**Apatite from Logrozan (Spain).** By A. VIVIER (*Compt. rend.*, **99**, 709—711).—Apatite from Logrozan occurs in regular hexagonal prisms, the bases of which are modified by pyramidal faces. The crystals are enclosed in an altered trachyte, and are generally more or less opaque, and yellowish or greenish in colour, with an uneven vitreous fracture. They contain numerous enclosures of lamellar specular hematite. Some of the crystals are as much as 25 mm. in length, but the apatite is also disseminated through the rock in microscopic crystals. The larger crystals, free from specular hematite, have the composition:—

Aluminium and beryllium phosphates .....	4.46
Calcium phosphate .....	89.54
Calcium chloride .....	0.77
Calcium fluoride (by diff.) .....	5.23

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100.00

C. H. B.

**Origin of the Phosphorites in the South-West of France.** By DIEULAFAIT (*Compt. rend.*, **99**, 440—443).—It has been urged that the author's theory of the formation of phosphorites, partially, if not entirely, by the action of percolating saline waters of the tertiary age, is not applicable to the phosphorites in the south-west of France, because this district was never covered by the sea during the tertiary period. In this district, however, there are many deposits of gypsum which undoubtedly belong to the tertiary period, and they contain in notable quantity lithium, strontium, manganese, zinc, copper, and boric acid, substances which the author has previously shown to be characteristic of the saline deposits and saliferous marls formed in modern seas. In all probability, therefore, the gypsums of the south-west of France, like those of the middle, and of the Paris basin, are products of the evaporation of saline waters.

If the excavation of the phosphoritic caverns and the deposition of phosphorites has been the work of saline waters of the tertiary period, it follows that a calcareous tract may only be expected to contain phosphorites when it is covered with deposits of tertiary age.

C. H. B.

**Minerals from the Metamorphic Rocks of Ouro Preto, Brazil.** By H. GORCEIX (*Jahrb. f. Min.*, 1884, **2**, Ref., 302—303).—



1. Crystals planted on quartz with cobalt oxide. The crystals are of a white colour,  $H. = 2-3$ , sp. gr. 2.3. They are soluble with difficulty in warm nitric acid, and have the following composition:—

$Al_2O_3$ .	$H_2O$ .	Total.
65.2	34.8	100.0

corresponding to the formula  $Al_2O_3 \cdot H_2O$ .

2. Crystals of *wavellite* in small geodes in black slate. The crystals are white or pale-green, acicular, with distinct cleavage.  $H. = 4$ . Sp. gr. 2.34. The analysis gave the following results:—

$P_2O_5$ .	F.	$Al_2O_3$ .	CaO.	MgO.	$H_2O$ .	Total.
33.0	3.6	36.1	0.3	0.2	26.2	99.4

3. *Pyrophyllite*. With the above minerals, acicular white, greenish or bluish crystals occur; sometimes accompanied by disthene. The mineral has a pearly lustre and low hardness. Sp. gr. 2.76. The analyses gave the following results:—

$SiO_2$ .	$Al_2O_3$ .	FeO.	CaO.	$H_2O$ .	Total.
65.3	28.0	1.7	0.4	5.5	100.9

B. H. B.

**Empholite.** By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1884, 2, Ref., 317—318).—The new mineral from Hörsjöberg, Sweden, formerly regarded as diaspor, gave on analysis the following results:—

$SiO_2$ .	$Al_2O_3$ .	MgO.CaO.FeO.	$H_2O$ .
52.3	30.5	3.4	13.8

The mineral is insoluble in acids,  $H. = 6$ . It is found in the quartzose, disthene, and muscovite schists.

B. H. B.

**The Potash-soda-felspars of Silesia.** By A. BEUTELL (*Jahrb. f. Min.*, 1884, 2, Ref., 319—324).—In an exhaustive paper on this subject, the author gives crystallographical descriptions and chemical analyses of the following felspars: microcline from the granitite of Schwarzbach and Grünbusch in the Riesengebirge, albite from the granitite of Schwarzbach, microcline from the granitite of Striegau, albite from the same locality, microcline from the granite vein of Lampersdorf and Leutmannsdorf in the Eulengebirge, and albite from Reichenbach.

B. H. B.

**Minerals from a Chromite Deposit.** By A. ARZRUNI (*Jahrb. f. Min.*, 1884, 2, Ref., 303—304).—The minerals were found near the Kassli smelting-works in the Ural. In fissures in the chromite, crystals of *kämmererite* occur; they are not violet, but of a bluish-green colour. Crystals of *perowskite* and *rutile* also occur, the latter containing chromium. This is probably due to enclosed *kämmererite*.

B. H. B.

**Magnesian Epidote.** By DAMOUR and DES-CLOIZEAUX (*Jahrb. f. Min.*, 1884, 2, Ref., 317).—On lapis lazuli from the Baikal Lake, mixed with dolomite and iron pyrites, small white or yellowish transparent

crystals were observed, the optical and crystallographical properties of which are those of epidote. The crystals scratch glass, are infusible before the blowpipe, and contain silica, alumina, magnesia, and traces of lime. The name picro-epidote is suggested for this epidote.

B. H. B.

**Schuchardtite.** By G. STARKL (*Jahrb. f. Min.*, 1884, 2, Ref., 305).—This mineral is of an apple-green colour, soft, and is disintegrated by water. Heated at 300° it loses 4·477 per cent. of water; in the desiccator it loses 1·6 per cent. Sp. gr. 2·339. The analysis gave the following results:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	NiO.	FeO.	CaO.
I.	33·281	14·616	3·825	5·678	3·561	1·472
II.	33·886	14·882	3·905	5·782	3·617	1·499
III.	33·214	15·093	2·605	6·106	3·517	1·824
	MgO.		H <sub>2</sub> O.		Total.	
I.	23·723		13·907		100·063	
II.	24·155		12·366		100·092	
III.	24·747		12·894		100·000	

I is the analysis of fresh material; II that of the substance dried at 100°, and III the calculated percentage composition. From the analysis is deduced the empirical formula—

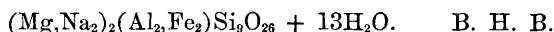


B. H. B.

**Groddeckite, a new Zeolite.** By A. ARZRUNI (*Jahrb. f. Min.*, 1884, 2, Ref., 318—319).—The groddeckite crystals cover calcite crystals which are planted on a breccia of a greenish-grey siliceous rock. In addition to calcite, quartz crystals, galena, and magnetic pyrites were observed. Only one specimen from St. Andreasberg has been met with, this is in the collection of the Clausthal School of Mines. The crystals are colourless and have a glassy lustre, H. = 2—3. Cleavage indistinct, prismatic. The crystals are very similar to those of gmelinite. The chemical composition is—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
51·2	12·0	7·7	1·1	3·3	4·5	20·2	100·0

corresponding with the formula—



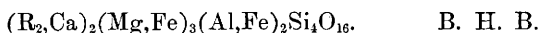
B. H. B.

**Constitution of the Amphiboles containing Alumina.** By R. SCHARIZER (*Jahrb. f. Min.*, 1884, 2, Mem., 143—157).—Schrauf published (*Jahrb. f. Min.*, 1883, 2, 84) an account of the action of heat on the hornblende from Jan Mayen, in which he stated that the thermal constants were different from those of actinolite. The author's chemical investigation now proves that the chemical constitution of actinolite is totally different from that of this hornblende. The analysis gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.
39·167	14·370	12·423	5·856	1·505	10·521
CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.	
11·183	2·013	2·478	0·396	99·912	

corresponding with the formula  $(R'_2, R'')_3(Al, Fe)_2Si_3O_{12}$ , the usual formula for amphiboles, free from alumina, being  $(Mg, Fe)_3CaSi_3O_{12}$ .

All amphiboles containing alumina must, according to the author, be mixtures of two terminal members, one being represented by the hornblende, rich in  $Al_2O_3$  and  $Fe_2O_3$ , from Jan Mayen, the other being actinolite free from alumina. For the monoclinic substance,  $R_3R_2Si_3O_{12}$ , the author adopts Breithaupt's name, *syntagmatite*, because the hornblende from Vesuvius, so termed, closely resembles the terminal member of this series of isomorphous mixtures, the hornblende from Jan Mayen. In order to prove the hypothesis that in the monoclinic division of the amphiboles two terminal members exist differing in chemical composition, actinolite of the type  $(Mg, Fe)_3CaSi_3O_{12}$ , a metasilicate and syntagmatite of the type  $R_3R''_2Si_3O_{12}$ , an orthosilicate, which mixed in variable proportions yields the hornblendes containing  $Al_2O_3$  and  $Fe_2O_3$ , a number of recent analyses were calculated. The results were distinctly in favour of the above hypothesis, and prove that three groups of amphiboles may be distinguished: the optically negative metasilicate, actinolite; the optically negative orthosilicate, syntagmatite; and the optically positive orthosilicate, pargasite, the composition of which may be expressed by the formula



**Leucite- and Nepheline-basalt from the Vogelsberg.** By H. SOMMERLAD (*Jahrb. f. Min.*, 1884, 2, Mem., 221—223).—In the collection belonging to the University of Giessen, the author found two interesting rocks in which the presence of leucite and nepheline had not previously been detected.

The leucite-basalt from Ulrichstein presented a compact greenish-black ground-mass, containing olivine and augite crystals. Under the microscope a finely crystalline ground-mass is seen, formed of minute augite crystals and magnetite grains, accompanied by occasional patches of leucite. Olivine, augite, and brown mica form porphyritic crystals. An analysis of the rock gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.
41·13	18·18	4·71	7·64	13·20	10·59
		K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
		1·59	2·00	1·74	100·78

The nepheline-basalt from the Ziegenstück near Herbstein is of a greyish-black colour. In the ground-mass, olivine grains and augite may be observed. Under the microscope, the principal mass is seen to consist of black angites, with magnetite grains and irregular patches of nepheline. The rock is a nepheline-basalt resembling the Taufstein rock.

B. H. B.

**A Pegmatite containing Large Crystals of Chlorophyllite.** By F. GONNARD (*Compt. rend.*, 99, 711—712).—A vein of pegmatite cutting through granite, about 10 kilom. from Montbrison, Loire, on the road between that place and St. Bonnet-le-Courreau, contains crystals of chlorophyllite as much as 6 cm. in length and about 3 cm. in diameter. Some are very dark-green, with a fracture which is vitreous in some parts, dull in others. These crystals seem to pass into fahlunite. Others are greenish, greenish-grey, or pearly-grey, and cleave very easily along the basal plane; sp. gr. 2·77. The pegmatite also contains crystals of white microcline, which have the rare face *h* very well developed. These crystals have a reddish tinge, and consist of thin laminæ united along the direction *h*, but covered with a thin layer of the same substance which masks the striæ.

C. H. B.

**Chemical Composition of Augites from Phonolites and Similar Rocks.** By P. MANN (*Jahrb. f. Min.*, 1884, 2, Mem., 172—205).—The author has isolated and analysed the augites from a number of phonolites and other rocks rich in alkalis. The rocks employed were phonolite from Elfdalen, leucitophyre from Rieden, hauynophyre from Melfi. Of these rocks, the two latter contain augite only, whilst in the two former some hornblende also occurs, but in such small quantity that sufficient material for analysis could not be obtained. The augites from all the rocks examined were proved to contain alkalis, those from the phonolites proper to a much greater extent than those from the leucite and hauyn rocks. All the analyses give a percentage of silica much too low for the amount of alkalis present, thus rendering very probable the presence of the silicate  $R_2R'''SiO_6$ , as suggested by Doelter. The extinction angle increases in direct proportion to the percentage of iron and alkalis. This is shown in the following table:—

	Fe <sub>2</sub> O <sub>3</sub> .	Total alkalis.	Extinction angle.
Melfi .....	12·67	1·99	39°
Rieden .....	19·52	3·35	30
Elfdalen .....	22·44	9·36	12
Hohentwiel .....	26·35	13·33	10

B. H. B.

### Organic Chemistry.

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**Exchange of Chlorine, Bromine, and Iodine between Organic and Inorganic Compounds.** By R. BRIK (*Annalen*, 225, 146—170).—These experiments were made to ascertain the influence exerted by the nature of the element contained in any inorganic haloid compound on the exchange of halogens with an organic haloid

derivative. The organic compounds employed were ethyl iodide, isobutyl chloride, benzyl chloride, and ethyl monochloracetate, the inorganic compounds were selected from the halogen compounds of the alkaline earths, of the heavy metals, and of arsenic, antimony, and bismuth. The mixtures were heated in vessels provided with a reflux apparatus, except when otherwise mentioned.

Calcium chloride and ethyl iodide do not react at the boiling point. Barium chloride and ethyl iodide react very slightly at  $140^{\circ}$ . Barium iodide and isobutyl chloride do not react on boiling. Barium iodide and ethyl monochloracetate exchange their halogens completely at the temperature of the water-bath. Barium iodide and benzyl chloride give a partial interchange. Cupric chloride and ethyl iodide do not react when boiled together, but on heating with alcohol at  $150$ — $160^{\circ}$  complete interchange is effected. Zinc iodide and ethyl monochloracetate react readily and nearly completely at  $90$ — $100^{\circ}$ . Zinc iodide and benzyl chloride react on mixing, the interchange becoming complete at  $45$ — $50^{\circ}$ . Zinc iodide and isobutyl chloride do not react when boiled together. Cadmium chloride and ethyl iodide do not react when boiled together, but partial interchange is effected by heating at  $130$ — $140^{\circ}$  in sealed tubes with alcohol. Cadmium bromide suffers partial interchange when boiled with either benzyl chloride or ethyl monochloracetate, but does not react with ethyl iodide. Cadmium iodide gives but a slight interchange with ethyl monochloracetate, reacts readily but not completely with benzyl chloride, and does not react with isobutyl chloride except in sealed tubes at  $135^{\circ}$ , when decomposition-products are formed. Thallium chloride and ethyl iodide do not react. Thallium iodide and ethyl monochloracetate give a partial reaction in presence of alcohol. Lead chloride and ethyl iodide do not react, but in sealed tubes at  $150$ — $160^{\circ}$  in presence of alcohol, nearly complete interchange is effected. Lead iodide and benzyl chloride do not react unless heated at  $150$ — $160^{\circ}$  in presence of alcohol, when a partial reaction occurs. Arsenious bromide reacts completely with either benzyl chloride or ethyl monochloracetate at  $140$ — $145^{\circ}$  in presence of alcohol. Antimonious bromide gives a complete interchange with either ethyl iodide or ethyl monochloracetate at  $140$ — $145^{\circ}$  in presence of alcohol. Bismuth bromide and ethyl iodide give a partial interchange at  $150$ — $160^{\circ}$  in presence of alcohol. Bismuth bromide and ethyl monochloracetate heated with alcohol at  $140^{\circ}$  give decomposition-products.

A. J. G.

**Exchange of Chlorine, Bromine, and Iodine between Inorganic and Organic Compounds.** By B. KÖHNLEIN (*Annalen*, **225**, 171—185).—This paper is essentially a continuation of Brix's (preceding Abstract), from which it differs in the use of a much larger number of metallic compounds; in the employment, as far as possible, of the same temperature ( $145$ — $150^{\circ}$  for four hours) in all cases, so as to obtain comparable results; and in the avoidance of the use of alcohol, which in many cases vitiates the results.

Lead iodide and isobutyl chloride react to a very slight extent; with lead chloride and ethyl iodide, on the contrary, nearly complete interchange occurs. Antimonious chloride and ethyl iodide exchange their

halogens completely. Antimonious bromide and ethyl monochloracetate react partially; antimonious bromide and ethyl iodide react completely. Antimonious iodide and isobutyl chloride react with decomposition, butylene being formed. Arsenious chloride and ethyl iodide undergo complete interchange. Arsenious bromide does not react with isobutyl chloride; it reacts partially with ethyl monochloracetate; it does not react with ethyl iodide unless the temperature is raised to 150—160°, when complete interchange takes place; it reacts completely with isopropyl iodide. Arsenious iodide scarcely reacts with ethyl monochloracetate, and does not react with isobutyl chloride. Phosphorous chloride and ethyl iodide do not react. Phosphorous iodide does not react with ethyl monochloracetate in open vessels at 143°, although complete decomposition occurs in sealed tubes at 150°; it does not react with isobutyl chloride at 140°, but complete decomposition occurs at 160—170°; it reacts with propyl chloride with decomposition at 150°. Stannous chloride, or stannic chloride, and propyl iodide react nearly completely, whilst stannous iodide scarcely reacts with propyl chloride. Zinc chloride, or cadmium chloride, and propyl iodide give a nearly complete reaction. Propyl iodide suffers decomposition if heated with titanium chloride. Ferrous iodide or chloride gives practically no reaction with the corresponding propyl compounds. Manganous iodide and propyl chloride exchange their halogens nearly completely; manganous chloride and propyl iodide do not exchange, but the propyl compound suffers partial decomposition. Cobalt chloride and propyl iodide react slightly; cobalt iodide and propyl chloride scarcely react. Nickel chloride and propyl iodide, and nickel iodide and propyl chloride respectively are practically without action on one another. Thallium chloride and propyl iodide react partially. Magnesium chloride and propyl iodide do not react. Calcium iodide and propyl chloride give a complete interchange. Strontium iodide and propyl iodide exchange partially, whilst strontium chloride and propyl iodide do not react. Barium chloride and propyl iodide are without action on one another.

The author draws the following conclusions as to these reactions:—K, Mg, Ca, Sr, Ba, Al, Mn, and Co unite by preference with chlorine rather than with bromine and iodine, and with bromine rather than with iodine (under some circumstances Sr, Ba, and Co gives light interchanges in the opposite direction). Zn, Cd, Tl, Bi, Fe, and Ni show no constant rule of interchange. Cu, Ag, Hg, Sn, Pb, As, and Sb unite by preference with iodine rather than with bromine or chlorine, and with bromine rather than with chlorine.

A. J. G.

**Action of Chlorine on Organic Compounds in Presence of Inorganic Chlorides.** By A. G. PAGE (*Annalen*, 225, 196—211).—Some years ago Aronheim showed that the presence of molybdenum pentachloride greatly facilitated the chlorination of aromatic compounds, but, from some preliminary experiments, did not appear to have the same effect on the chlorination of fatty bodies (this *Journal*, 1876, i, 309). The author has continued this investigation and extended it to the employment of other inorganic chlorides.

Chlorine does not act on acetic chloride even in presence of molyb-

denum pentachloride. The chlorination of butyric chloride and of ethylene chloride is actually hindered by the presence of molybdenum chloride. Molybdenum trichloride does not assist chlorination below the temperature ( $70^{\circ}$ ) at which it is converted into pentachloride. Of the numerous other chlorides experimented with, the following only were found to assist chlorination:  $\text{Fe}_2\text{Cl}_6$ ,  $\text{Al}_2\text{Cl}_6$ ,  $\text{TiCl}_4$ , and  $\text{TiCl}_3$ ; the chlorinating action of  $\text{MoCl}_5$  and  $\text{SbCl}_5$  is already well known.

As regards the action of these bodies in assisting chlorination, the author regards the view that a molecular compound is formed between the metallic chloride and the substance being chlorinated, which compound is in the second place decomposed by chlorine with formation of hydrochloric acid and a chlorinated product, as being more probable than that which is based on an alternate reduction and chlorination of the inorganic chloride.

Chlorine has no action on nitrobenzene, but in presence of ferric chloride at ordinary temperatures it converts it into the dichloronitrobenzene [ $\text{Cl} : \text{Cl} : \text{NO}_2 = 1 : 4 : 3$ ], and at  $100^{\circ}$  into the tetrachloronitrobenzene [ $\text{Cl} : \text{Cl} : \text{NO}_2 : \text{Cl} : \text{Cl} = 1 : 2 : 3 : 4 : 5$ ], whilst at higher temperatures it converts it completely into perchlorobenzene.

Whilst chlorine acting alone on alcohol converts it chiefly into chloral alcoholate; in the presence of ferric chloride, it converts it into a mixture of chloral and (very little) chloral hydrate. A. J. G.

**Anthemene, a Hydrocarbon obtained from Roman Chamomile.** By L. NAUDIN (*Bull. Soc. Chim.*, **41**, 483—488).—From the flowers of chamomile (*Anthemis nobilis*), the author has obtained two white crystalline substances, one of which appears to be a hydrocarbon. The flowers are exhausted completely with light petroleum, the solution thus obtained is evaporated to one-ninth of its bulk, and the liquid residue allowed to stand. In a few days, groups of white crystals of the new substance separate out, and in the mother-liquid are substances previously described by Demarçay, Fittig, and Kopp. The crystals were purified by recrystallisation from ether and light petroleum, and were found to consist of two substances. As one of them is twenty-four times as soluble in absolute cold alcohol as the other, they were separated by dissolving in hot alcohol, boiling with animal charcoal, and filtering. Anthemene crystallises out on cooling, and the second substance melting at  $188$ — $189^{\circ}$ , the investigation of which has not yet been completed, remains in solution. The process of separation was repeated twelve times. The yield is very small, for from 1 kilo. of the flowers the author only obtained 1.5 grams of anthemene and 4.5 grams of the second substance.

Anthemene crystallises in slender microscopic needles melting at  $63$ — $64^{\circ}$ , and boiling at about  $440^{\circ}$  without much decomposition; sp. gr. 0.942 at  $15^{\circ}$ . It is insoluble in water, but soluble in ether, petroleum, carbon bisulphide, and chloroform, and soluble in hot absolute alcohol, but almost insoluble in cold (at  $25^{\circ}$ , 1 litre dissolves 0.333 gram). The vapour-density by V. Meyer's method in the vapour of sulphur was 127 (theor. 131). The results of analysis give the percentage of carbon 83.80, and of hydrogen 14.40, showing a loss of 1.80. Schlützenberger, who repeated the analyses, obtained similar



results, and the author cannot account for this loss, as the compound appears to be pure and to contain no oxygen. It appears to be of the series  $C_nH_{2n}$ , and to be a  $\beta$ -octadecene (C 85·82, H 14·18).

A. B.

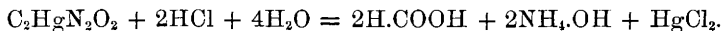
**Diethoxymethane, and Preparation of Methylene Dichloride.**

By W. H. GREENE (*Chem. News*, 50, 75—76).—The author has made diethoxymethane from sodium ethylate and methylene dichloride. Sodium, in equal molecular proportion, is added gradually to a mixture of methylene chloride with excess of absolute alcohol contained in a flask fitted with reflux condenser; when all the sodium has been added, the mixture is heated for an hour, and then distilled. The product is fractioned, and all which passes over below  $78^\circ$  is shaken with calcium chloride solution, the upper layer separated, dried, and rectified, when pure diethoxymethane is obtained boiling at  $86$ — $89^\circ$ . It is an ethereal liquid with penetrating mint-like odour, boiling at  $89^\circ$  under 769 mm. pressure. Its sp. gr. at  $0^\circ$  is 0·851. It is slightly soluble in water, and miscible in all proportions with alcohol and ether.

The following is recommended as the most convenient process for preparing methylene chloride. A mixture of zinc and chloroform with much alcohol is treated with a small quantity of hydrochloric acid in a flask fitted with a condenser; heat is developed and chloroform and methylene chloride distil over. When the reaction subsides, more hydrochloric acid is added, and a gentle heat is applied until near the completion of the operation, which is stopped when the alcohol commences to come over in large quantities. The distillate is rectified, the portion coming over below  $53^\circ$  being retained, whilst the residue is again treated with zinc, &c. This operation is repeated several times, and ultimately, by numerous careful rectifications of the product boiling below  $53^\circ$ , pure methylene chloride boiling at  $40$ — $41^\circ$  is obtained.

D. A. L.

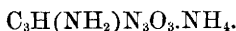
**Mercury Fulminate.** By A. EHRENBURG (*J. pr. Chem.*, 30, 38—68).—Carstanjen and the author have shown (Abstr., 1882, 816) that when mercury fulminate is decomposed with aqueous hydrochloric acid, it yields its nitrogen as hydroxylamine hydrochloride. A further examination of this reaction has proved that both carbonic oxide and carbonic anhydride are formed. The quantity of these compounds produced is but small, more especially when the decomposition is effected in absence of air; and it appears that they owe their origin to the decomposition of formic acid, which the author has shown is produced by the action of aqueous hydrochloric acid on mercury fulminate. The reaction taking place may be represented as follows:—



In the hope of realising the following decomposition, and thus obtaining fulminic acid,  $C_2HgN_2O_2 + 2HCl = HgCl_2 + C_2H_2N_2O_2$ , the author passed dry hydrochloric acid gas into perfectly dry ether containing mercury fulminate in suspension. Mercuric chloride is produced, and the ether holds in solution a compound which undergoes spontaneous decomposition, most probably fulminic acid. If this ethereal solution is carefully added to aqueous ammonia, and the

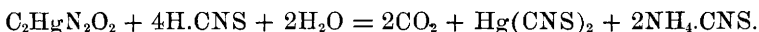
ethereal solution separated from the aqueous solution, the latter contains a yellow solid which is sparingly soluble in cold water, but soluble in hot water, from which it may be obtained in yellowish needles. The analysis of this compound shows it to be  $C_3H_4N_4O_2$ ; it forms with silver nitrate a compound,  $(C_3H_4N_4O_2)_2AgNO_3$ , insoluble in cold water, and with an ammoniacal solution of copper oxide the compound  $(C_3H_4N_4O_2)_2CuO(NH_3)_2$ , which is obtained as a light blue granular precipitate. From the ammoniacal solution from which the above compound was obtained, the author has isolated an acid isomeric with fulminuric acid, to which the name *Isifulminuric acid* is given. It is easily soluble in water, from which it separates in ill-defined crystals; absolute alcohol dissolves it easily, and by cooling the hot saturated solution it is obtained as a white powder. With silver nitrate, its aqueous solution gives a white amorphous precipitate of  $C_3H_2N_3O_3Ag$ , but yields no precipitates with ammoniacal solutions of copper oxide, lead acetate, or mercuric chloride. The silver, ammonium, and barium salts of this acid are described.

Together with this acid, there is formed a small quantity of a compound more easily soluble in ether than isofulminuric acid, which is most probably the ammonium salt of amidofulminuric acid,



Its aqueous solution gives precipitates with silver nitrate, lead acetate, and copper sulphate, and a blood-red to brownish-red coloration with ferric chloride.

Thiocyanic acid reacts with mercury fulminate in a manner analogous to aqueous hydrochloric acid, mercuric thiocyanate, ammonium thiocyanate, and carbonic anhydride are produced. the production of the ammonium salts arising from the instability of hydroxylamine thiocyanate. The reaction may be represented thus:—



The action of ammonium thiocyanate on mercury fulminate is analogous to the action of the chlorides of the alkali metals, but is more energetic; it may be expressed as follows:—



P. P. B.

**Mercury Fulminate.** By L. SCHOLVIEN (*J. pr. Chem.*, **30**, 91—92).—A solution containing sodium fulminate is formed by treating mercury fulminate suspended in water with sodium amalgam. When this solution is decomposed with dilute sulphuric acid and shaken up with ether, the ethereal solution is found to contain two acids of the composition  $HCNO$ . The less soluble of these crystallises from ether in colourless needles melting at  $85^\circ$ ; it is soluble in lukewarm water, but is decomposed by boiling water. It forms a red insoluble silver salt, a dark yellow mercuric salt, and light yellow lead salt. Its solutions yield a deep red coloration with ferric chloride. Decomposed by hydrochloric acid, it yields hydroxylamine. The more soluble isomeride may be crystallised from hot water, yields no

coloration with ferric chloride, and forms no insoluble metallic salts.

The aqueous solution of sodium fulminate gives a precipitate of silver fulminate with silver nitrate, which when treated with metallic chlorides and aniline hydrochloride forms double salts. It is decomposed by ethyl iodide, and with potassium sulphide yields an easily explosive compound.

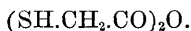
Mercury fulminate and thiocarbamide yield carbonic anhydride, mercuric sulphide, carbamide, a compound thiocarbamide and mercuric thiocyanate. P. P. B.

**Rhodanic Acid.** By M. NENCKI and BOURQUIN (*Ber.*, 17, 2277—2282).—10 grams of rhodanic acid,  $C_3H_3NS_2O$ , dissolved in 50 c.c. of 90 per cent. alcohol, were mixed with 30 grams of strong sulphuric acid and heated on a water-bath; 15 grams of benzaldehyde were then added gradually. On cooling, or on the addition of water, *benzylidene-rhodanic acid*,  $C_{10}H_7NS_2O$ , crystallises out. When purified this acid forms yellow needles, melting at  $200^\circ$  (uncorr.). It gives crystalline salts with the alkalis, very easily soluble in alcohol and water, less so in concentrated alkalis. It forms a yellowish-green *silver salt*,  $C_{10}H_6AgNS_2O$ , and an amorphous *lead salt*. The reaction takes place according to the equation



Acetaldehyde or its ammonia-compound similarly yields *ethylidene-rhodanic acid*,  $C_5H_5NS_2O$ . This substance forms small yellow needles, melting at  $147-148^\circ$ . It is very sparingly soluble in water, easily in alcohol. It gives a yellow amorphous *lead salt*. Both of these compounds are decomposed when heated with alkalis, the aldehydes being reformed and the rhodanic acid further decomposed. Salicylaldehyde and parahydroxybenzaldehyde also form similar condensation-compounds, but these have not been investigated.

When heated with water at  $200^\circ$  in closed tubes, rhodanic acid is split up into carbonic anhydride, sulphuretted hydrogen, and ammonium thioglycollate. When warmed with alkalis, it is readily decomposed, potassium thiocyanate and a crystalline potassium (or sodium) salt sparingly soluble in alcohol being the products. The acid of which this is the salt appears to have the composition of an anhydride of thioglycollic acid, and to be of the formula



This acid is now undergoing investigation.

As this formation of thiocyanic acid by the action of alkalis takes place at so low a temperature, there can be little doubt that the thiocyanic group is already present in rhodanic acid. The formula  $S:C<\overset{SH.CH_2}{\underset{-NH_2}{}}>CO$ , proposed by Liebermann, is therefore very improbable, and that originally proposed by Nencki,  $SH.CH_2.CO.S.CN$ , is in all probability the correct one. L. T. T.

**Circular Polarisation of Dextrose.** By B. TOLLENS (*Ber.*, 17, 2234—2238).—In continuation of his investigations with cane-sugar

(Abstr., 1884, 1285), the author has now examined very dilute solutions of dextrose. He finds that here, as in the case of cane-sugar, no increase of rotation takes place, but that the same formula may be employed for calculating the rotation whatever the degree of concentration of the solution. The dextrose employed was very carefully purified by the method recommended by Soxhlet, and was purer than that previously used. The author has therefore slightly amended his old formulæ, which now become—

$$A \text{ (for anhydrous dextrose) } [\alpha]_D = 52.50^\circ + 0.018796P + 0.00051683P^2.$$

$$B \text{ (for dextrose hydrate) } [\alpha]_D = 47.73^\circ + 0.015534P + 0.0003883P^2.$$

The following table gives a comparison between the results actually found with a Landolt-Laurent polarimeter and those calculated:—

Weight of sugar in 100 grams solution. P.	Rotation for $[\alpha]_D$ .		Difference.
	Found.	Calculated.	
1.4978	52.407°	52.532°	— 0.125°
1.7933	52.289	52.537	— 0.248
2.7533	52.370	52.556	— 0.186
7.6042	52.691	52.673	+ 0.018
10.0992	52.738	52.742	+ 0.004
10.2567	52.636	52.747	— 0.111
17.5982	52.991	52.991	— 0.000

L. T. T.

**Non-identity of Arabinose and Galactose.** By E. O. v. LIPPMANN (*Ber.*, 17, 2238—2240).—The author confirms Scheibler's results as to the non-identity of these two compounds. Galactose forms large, hard, well-formed prisms melting at 148°; arabinose long, fragile needles melting at 160°. Arabinose has a sweeter taste than galactose. The rotation of arabinose in a 10 per cent. solution is  $[\alpha]_D = +105.4^\circ$ ,  $[\alpha]_j = +118^\circ$  of galactose,  $+81.5^\circ$  and  $+92^\circ$  respectively. Arabinose shows no birotation, galactose does; a fresh solution having given  $[\alpha]_D = 134.5^\circ$ . Fermentation is easily set up in solutions of galactose by means of yeast, but arabinose cannot be fermented. When oxidised with nitric acid, arabinose yields only oxalic acid, while galactose forms mucic acid. The reducing power of arabinose for Fehling's solution is also greater than that of galactose.

With regard to the existence of the four arabinoses described by C. O'Sullivan (*Trans.*, 1884, 41, *et seq.*), the author calls attention to the existence of unstable intermediate products (such as cerasinose, which is gradually converted, even in the crystalline form, into arabinose) analogous to these compounds, and suggests that the various arabinoses may actually exist, and not be mere mixtures of arabinose with galactose as Scheibler believes.

L. T. T.

**Influence of Temperature and Concentration of Hydrochloric Acid on the Rate of Inversion of Saccharose. (II).** By F.

URECH (*Ber.*, 17, 2165—2178). The author refers to his previous experiments (*Abstr.*, 1883, 174), the results of which he now represents by means of curves and tables. A. K. M.

**"Hydrate of Carbon" from Cast Iron.** By ZABOUDSKY (*Bull. Soc. Chim.*, 41, 424—428).—A very pure specimen of Swedish specular cast iron, free even from traces of graphite, phosphorus, or sulphur, but containing 0.23 per cent. of silicon and 4.1 per cent. of combined carbon, when treated with a mixture of copper sulphate and sodium chloride yielded 5.72—5.79 per cent. of a "hydrate of carbon," which contained C 71.6; H<sub>2</sub>O 26.9; siliceous ash 1.25 per cent. These results approximate to the formula C<sub>12</sub>H<sub>6</sub>O<sub>3</sub>. Treatment of the steel with other reagents, silver nitrate, mercuric chloride, atmospheric air, and by Weyl's method, gave rise to the formation of an analogous substance. The hydrate is not changed when heated in a closed tube to 150°, and although it gradually loses weight when further heated, at 325° losing carbon as well as water, it retains hydrogen and oxygen even after being heated in a bath of metallic antimony. Heated in a current of hydrogen, the compound lost considerably in weight, but after prolonged action the residue still contained hydrogen to the extent of nearly 3 per cent. The compound is insoluble in water, alcohol, ether, sulphuric and hydrochloric acids. It is completely dissolved by warm nitric acid, forming a substance which probably has the formula C<sub>24</sub>H<sub>16</sub>(NO<sub>2</sub>)O<sub>12</sub>. This body dissolves easily in alcohol and in nitric acid. It is insoluble in ether, but is dissolved by alkalis, forming a dark brown solution, from which hydrochloric acid precipitates the original compound apparently unchanged. This nitro-compound gives an odour of hydrogen cyanide when heated. Chlorine, bromine, and iodine also act on the hydrate of carbon; the iodo-derivative probably has the formula C<sub>60</sub>H<sub>20</sub>IO<sub>15</sub>. W. R. D.

**Angelic and Tiglic Acids.** By F. BEILSTEIN and E. WIEGAND (*Ber.*, 17, 2261—2263).—The authors have examined the products produced by the oxidation of these acids with potassium permanganate, in the hope of learning something of their respective constitutions. Aldehyde and acetic acid were formed in both cases; the only difference being that with angelic acid a very small quantity of a non-volatile acid yielding an amorphous barium salt was formed.

The acids were prepared by Kopp's process from roman oil of chamomile (*Abstr.*, 1879, 454), and their ethers were also made.

*Ethyl angelate* is an aromatic liquid boiling at 141.5° and having a sp. gr. of 0.9347 at 0°.

*Ethyl tiglate* boils at 152° and has a sp. gr. of 0.9425 at 0°.

L. T. T.

**Halogen-derivatives of Ethyl Levulinate.** By M. CONRAD and M. GUTHZEIT (*Ber.*, 17, 2285—2287).—With reference to the communication of Hell and Kehrler (*Abstr.*, 1884, 1297), on the action of bromine on levulinic acid, the authors publish this account of some similar work carried out simultaneously and independently by themselves.

*Ethyl monobromolevulinate*, C<sub>5</sub>H<sub>11</sub>BrO<sub>3</sub>, was obtained by gradually

adding 16 grams of bromine to 14.4 grams of ethyl levulinate diluted with 25 c.c. of ether, the whole being kept cool by means of ice. It boils with partial decomposition at  $240^{\circ}$ , and has a sp. gr. of 1.439 at  $15^{\circ}$  compared with  $H_2O$  at the same temperature. It enters into reaction with ethyl sodomalonate, forming a colourless oil of the formula  $(COOEt)_2CH.C_6H_5O.CO OEt$ , boiling at  $280-285^{\circ}$ , and having the sp. gr. 1.097 at  $15^{\circ}$ . Ethyl monobromolevulinate absorbs more bromine and, as end-product, the authors obtained a mixture of the di- and tri-bromo-derivatives. Ethyl monochlorolevulinate, prepared in a similar manner, is a colourless oil insoluble in water. It boils at  $225-230^{\circ}$ , and has the sp. gr. 1.196 at  $15^{\circ}$ . L. T. T.

**Adipic Acid.** By W. DIETERLE and C. HELL (*Ber.*, 17, 2221—2228).—In continuation of the researches of Gantter and Hell on suberic and azelaic acids, the authors have investigated adipic acid, the third of the higher dibasic acids obtained in the oxidation of fats.

The adipic acid was prepared from the mother-liquors obtained in the preparation of suberic acid from castor-oil and other fats.

Adipic acid is much less soluble in ether than suberic acid, but much more soluble in water. The two acids can be therefore easily separated by successive crystallisations from these two solvents. The adipic acid thus obtained is still slightly yellow, and is purified by crystallisation from strong nitric acid or by conversion into its salts.

Adipic acid melts at  $148-149^{\circ}$ , and solidifies to a crystalline fibrous mass. At  $15^{\circ}$ , 100 parts of water dissolve 1.44 parts of acid; 100 parts of ether, 0.633 part of acid. Adipic acid has a very great tendency to form supersaturated solutions. It is not volatile in steam, but can be distilled alone without decomposition. It is only attacked by bromine above  $150^{\circ}$ , but it about 0.3 per cent. amorphous phosphorus is added, bromination takes place at the temperature of the water-bath.

The *potassium salt*,  $K_2C_6H_8O_4$ , forms deliquescent crystals; the *sodium salt*, mother-of-pearl-like scales containing  $\frac{1}{2}H_2O$ , and easily soluble in water. The *ammonium salt* is much more stable than the corresponding salts of suberic and azelaic acids, and may be evaporated without decomposition. It crystallises in scales, and at  $14^{\circ}$ , 100 parts of water dissolve 39.97 of the salt: at  $100^{\circ}$ , it loses half its ammonia, the acid salt being formed, and at  $120-150^{\circ}$ , the rest of the ammonia escapes and the pure acid is left. The *barium salt* is less soluble in hot than in cold water, 100 parts of water dissolving 12.04 parts of salt at  $12^{\circ}$ , and only 7.47 at  $100^{\circ}$ . The *strontium salt* forms prismatic prisms containing  $\frac{1}{2}H_2O$ : 100 parts of water dissolve 13.61 parts of the anhydrous salt at  $14^{\circ}$ , and 2.72 at  $100^{\circ}$ . The *calcium salt* crystallises with  $1H_2O$ : 100 parts of water dissolve 4.02 parts of the anhydrous salts at  $13^{\circ}$ , 4.09 at  $17^{\circ}$ , and 1.20 at  $100^{\circ}$ . The *magnesium salt* crystallises with  $4H_2O$ : 100 parts of water dissolve 25.01 parts at  $15^{\circ}$ , and 21.71 at  $100^{\circ}$ . The *aluminium* and *ferric salts* form voluminous and almost insoluble precipitates. The *manganese salt* micaceous crystals containing  $2H_2O$ , or, if deposited at high temperatures,  $1H_2O$ : 100 parts of water dissolve 12.63 parts of the anhydrous salt at  $18^{\circ}$ , and 2.71 at  $100^{\circ}$ . The *nickel salt* yields apple-green scales

containing  $4\text{H}_2\text{O}$ , and only loses the last molecule completely at  $140^\circ$ : 100 parts of water dissolve 0.65 part of anhydrous salt at  $15^\circ$ , 4.07 parts at  $100^\circ$ . The *cobalt salt* forms pale red prisms containing  $4\text{H}_2\text{O}$ , which it loses at  $110^\circ$ : the anhydrous salt is of an intense bluish-violet colour: 100 parts of water dissolve 1.56 parts at  $15^\circ$ , 3.09 at  $100^\circ$ . The *zinc salt* crystallises with  $2\text{H}_2\text{O}$ : 100 parts of water dissolve 0.267 part at  $10^\circ$  and 0.217 at  $100^\circ$ . The *copper salt* forms a voluminous bluish-green precipitate: when this is quickly pressed and dried, it contains 1 mol.  $\text{H}_2\text{O}$ , but if allowed to remain under water takes up another mol.  $\text{H}_2\text{O}$  and then forms small deep blue crystals: 100 parts of water dissolve 0.024 part of the anhydrous salt at  $15^\circ$ , 0.029 at  $17^\circ$ , and 0.063 at  $100^\circ$ . The *lead salt* forms an anhydrous white precipitate: 100 parts of water dissolve 0.0206 part at  $12.5^\circ$ , 0.0217 at  $16^\circ$ , and 0.0217 at  $100^\circ$ . The *mercuric salt* forms an anhydrous crystalline precipitate: 100 parts of water dissolve 0.0287 part at  $11^\circ$ , 0.0125 at  $100^\circ$ . The *silver salt* is stable towards light, and forms small glittering scales: 100 parts of water dissolve 0.0166 part at  $14^\circ$ , and 0.0491 at  $100^\circ$ .

The salts of the heavier metals were mostly prepared by double decomposition. Precipitation often takes place very slowly in the cold, but is accelerated by stirring or heating the solution. The salts of adipic acid resemble those of suberic acid in many respects, but they are all more soluble than the latter.

L. T. T.

#### Normal Butylmalonic Acid: a New Isomeric Pimelic Acid.

By C. HELL and G. LUMPP (*Ber.*, 17, 2217—2220).—To prepare this acid, normal caproic acid is heated with bromine at  $130^\circ$ , the monobromocaproic acid obtained is converted into the ethyl salt, and this is boiled for one and a half to two days with a dilute alcoholic solution of pure potassium or sodium cyanide, the nitrile thus formed being saponified by boiling with aqueous potash. *Butylmalonic acid*,  $\text{C}_7\text{H}_{12}\text{O}_4$ , crystallises from water in thick prisms, melts at  $101.5^\circ$ , and is readily soluble in water, alcohol, and ether. On warming it or its salts with concentrated sulphuric acid, they assume a red to violet coloration. When butylmalonic acid is heated, it readily splits up into carbonic anhydride and caproic acid, the decomposition beginning at a little below  $140^\circ$ , and being complete at  $150^\circ$ ; the readiness with which this acid is decomposed distinguishes it from the pimelic acid obtained from fats, which may be distilled without decomposition. The *barium salt*,  $\text{C}_7\text{H}_{10}\text{O}_4\text{Ba}$ , crystallises in white anhydrous scales; solubility at  $24^\circ$ , 2.98 parts salt in 100 parts water, and apparently less soluble in hot than in cold water. The *lead salt*,  $\text{C}_7\text{H}_{10}\text{O}_4\text{Pb}$ , is precipitated in lustrous white crystalline scales, 100 parts of water dissolving at  $20^\circ$  only 0.0112 part salt. The *silver salt*,  $\text{C}_7\text{H}_{10}\text{O}_4\text{Ag}_2$ , forms a voluminous pulverulent precipitate, 0.119 part dissolving in 100 parts water at  $23^\circ$ . The *copper salt*,  $\text{C}_7\text{H}_{10}\text{O}_4\text{Cu}$ , forms blue scales containing 1 mol.  $\text{H}_2\text{O}$ .

A. K. M.

**Occurrence of Pimelic Acid amongst the Oxidation-products of Castor-oil.** By F. GANTTER and C. HELL (*Ber.*, 17, 2212—2217).—Arppe showed that the so-called pimelic acid obtained by the action

of nitric acid on oleic acid and fatty bodies was a mixture of adipic and suberic acids. The author has obtained it, however, in considerable quantity by the oxidation of castor-oil by nitric acid. The more sparingly soluble acids are first separated, and the syrupy mother-liquor is largely diluted with water, neutralised with chalk, filtered, and concentrated. The calcium salt obtained is decomposed with acid, when a partly oily and partly crystalline product separates, and may be purified by alternate treatment with ether and water. Pimelic acid, which may also be obtained by the oxidation of earth-nut oil, crystallises from water in clusters of large flat plates, which melt at  $105.5-106^{\circ}$ , and solidify to a crystalline mass, which suddenly falls to pieces with the slightest touch. The *barium salt*,  $C_7H_{10}O_4Ba \cdot H_2O$ , crystallises in white indistinct scales; the *lead salt*,  $C_7H_{10}O_4Pb$ , and the *silver salt*,  $C_7H_{10}O_4Ag_2$ , form white pulverulent precipitates; and the *copper salt*,  $C_7H_{10}O_4Cu$ , a green precipitate. The pimelic acid appears to be distinct from all the acids of the composition  $C_7H_{12}O_4$  hitherto described; its properties approximate most to those of Bauer and Schuler's isopimelic acid (from amylene bromide), but a more extended comparison of the two is necessary to decide the question of identity.

A. K. M.

**Chelidonic Acid.** By J. U. LERCH (*Monatsh. Chem.*, 5, 367—414)—The author refers to his previous work, and claims priority before Haitinger and Lieben (see next Abstract).

The ethyl salts were prepared by the usual methods; the *diethyl salt*,  $C_7H_2O_6Et_2$ , melts at  $62^{\circ}$ ; the *monethyl salt*, also formed by decomposition of the preceding, melts at  $182-184^{\circ}$ ; its lead and silver salts,  $C_7H_2O_6EtAg$ , are crystalline. The diethyl salt, dissolved in alcohol, gives with ammonia a yellow solution, and then white crystals, probably the amide of chelidonic acid,  $C_7H_2O_4(NH_2)_2$ . The yellow solution obtained by adding excess of potash to chelidonic acid is gradually decomposed, even at ordinary temperatures, into oxalic acid and acetone; the acid is also decomposed by bromine and chlorine, oxalic acid and substituted acetones being formed. Potash gradually added to water containing calcium chelidonate in suspension converts the whole into a stiff yellow jelly, without the formation of oxalic acid and acetone; it is a potassium calcium salt of *cheli-hydrionic acid* (xanthochelidonic acid of Haitinger and Lieben), and is more applicable for further preparation work than the easily decomposable potassium salt. The free acid can only be prepared with great difficulty; the gelatinous potassium calcium salt is treated with sulphuric acid, and fractionally extracted from ether; from the second and following ethereal extracts it is obtained as a pale yellow amorphous mass. By neutralising the gelatinous potassium-calcium salt with acetic acid, the calcium salt,  $C_7H_2O_7Ca_2$ , is obtained as a citron-yellow precipitate. Chelihydrionic acid neutralised with ammonia gives a red solution, from which a crystalline ammonium salt may be obtained. This red solution gives, with silver nitrate, a yellow precipitate,  $C_7H_3O_7Ag_3 + 4H_2O$ , which by boiling is converted into a brown precipitate,  $C_7H_3O_7Ag_4$ . If in the above the chelihydrionic acid be replaced by the gelatinous calcium potassium salt, silver



precipitates having the same colour are obtained; but they are double salts, viz., yellow,  $(C_7H_3O_7Ag_2)_2Ca + 4H_2O$ , and brown,  $(C_7H_3O_7Ag_3)_2Ca$ , whilst lead and barium solutions also produce yellow precipitates of the composition  $(C_7H_2O_7)_4Pb_5Ca_3 + 6H_2O$  and  $C_7H_2O_7BaCa$ ; the calcium potassium salt precipitated from its solution by alcohol has the composition  $(C_7H_2O_7)_2Ca_3K_2 + 2H_2O$ . Chelidhydronic acid has therefore the composition  $C_7H_6O_7$ , and contains three or four hydrogen-atoms that may be replaced by metals.

Chelidonic acid evaporated with ammonia gives the ammonium salt of *chelidammic acid*, whose salts are also formed by the action of ammonia on the chelidonates. Hydrochloric acid added to a solution of the ammonium salt produces a precipitate of the formula  $C_{14}H_{13}N_3O_{10}$ ; this is a compound of the free acid with its ammonium salt,  $C_7H_5NO_5 + C_7H_4NO_5 \cdot NH_4$ ; it seems to be monoclinic, and dissolves in 1576 parts of cold water. By boiling this substance with potash, and then acidifying, the compound  $C_7H_7NO_6$  separates; this is a hydrate of the free acid,  $C_7H_5NO_5 + H_2O$ ; it crystallises in rhombic prisms, and dissolves in 637 parts of cold water. *Ethyl chelidammate*,  $C_7H_3NO_5Et_2 + H_2O$ , melts at  $80-81^\circ$ , and becomes anhydrous in a vacuum. Although the acid contains only two acid hydroxyl-groups, it forms three classes of salts; the following are described:— $C_7H_3NO_5Pb(NH_4)$ ;  $(C_7H_2NO_5)_2Pb_3$ ;  $C_7H_3NO_5Pb$ ;  $C_7H_2NO_5PbAg$ ;  $(C_7H_2NO_5)_2Pb_2Ba + 3H_2O$ ;  $C_7H_2NO_5PbK + 3H_2O$ ;  $C_7H_3NO_5Ag_2$ ;  $C_7H_3NO_5Ca + 2H_2O$ ;  $(C_7H_2NO_5)_2Ca_3$ ;  $C_7H_2NO_5Ca(NH_4) + 2H_2O$ .

When chelidammic acid is treated with the halogens, it yields bi-substitution-products. *Bromochelidammic acid*,  $C_7H_3Br_2NO_5 + 2H_2O$ , forms large efflorescent crystals; its silver salt is  $C_7HBr_2NO_5Ag_2$ . *Chlorochelidammic acid*,  $C_7H_3Cl_2NO_5 + H_2O$ , forms long fibrous crystals; its silver and lead salts are  $C_7Cl_2NO_5Ag_3$  and  $(C_7Cl_2NO_5)_2Pb_3$ . *Iodo-chelidammic acid* is obtained by dissolving chelidammic acid in an alkali, saturating with iodine, and then acidifying; its formula is  $C_7H_3I_2NO_5$ .

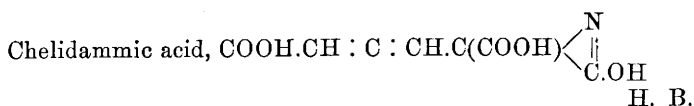
Chelidammic acid at  $250^\circ$  loses carbonic anhydride, and there remains a crystalline mass of *chelamide* (*hydroxypyridine*),  $C_5H_5NO$ , melting at  $95-96^\circ$ , and therefore different from the hydroxypyridines of Öst, of Fischer and Körner, and of König and Geigy, which melt at  $148^\circ$ ,  $123.5^\circ$ , and  $107^\circ$ . When crystallised from water, it has the formula  $C_5H_5NO + H_2O$ . Heated with zinc-dust, it yields pyridine. The double salts  $(C_5H_5NO)_2 \cdot H_2P_2Cl_6 + H_2O$ ;  $C_5H_5NO \cdot NO_3H \cdot AgNO_3$ ;  $C_5H_5NO \cdot HgCl_2$ ; and the hydrochloride,  $C_5H_5NO \cdot HCl$ , are described.

Chelidonic acid is also acted on by aniline, producing a crystalline body. Aniline chelidonate when heated evolves carbonic anhydride, and leaves a crystalline residue which after recrystallisation from water, has the composition  $C_{11}H_9NO + 2H_2O$ ; this anilide, however, does not form either single or double salts.

Following is a discussion of the constitution of these bodies; the following formulæ are advocated:—

Chelidonic acid,  $COOH \cdot CH : C : CH \cdot C(COOH) < \overset{O}{\underset{CO}{\curvearrowright}}} >$ .

Chelidhydronic acid,  $COOH \cdot CH : C : CH \cdot C(OH)(COOH)_2$ .



**Chelidonic Acid.** By HAITINGER and A. LIEBEN (*Monatsh. Chem.*, **5**, 339—366).—Reference is made to all previous work on the subject. Lietzenmayer's method for isolating the acid was used. The free acid suspended in alcohol and hydrochloric acid gas passed through, the solution evaporated and the residue dissolved in alcohol deposits monethyl chelidonate, the diethyl salt remaining in solution. The *diethyl salt*,  $\text{C}_7\text{H}_{10}\text{O}_6\text{Et}_2$ , forms crystals melting at  $62.7^\circ$ . The *monethyl salt*,  $\text{C}_7\text{H}_8\text{O}_6\text{Et}$ , is crystalline, melts at  $223\text{--}224^\circ$ , and its alcoholic solution has an acid reaction. Chelidonic acid is dibasic, and not tribasic.

It has been previously shown that when chelidonic acid is heated with alkalis or, much better, alkaline earths, it yields acetone and oxalic acid. This has been rigorously confirmed, and it is also shown that the reaction proceeds exactly according to the equation  $\text{C}_7\text{H}_4\text{O}_6 + 3\text{H}_2\text{O} = 2\text{C}_2\text{O}_4\text{H}_2 + \text{C}_3\text{H}_6\text{O}$ .

When chelidonic acid is treated with potash solution, a transient yellow coloration is produced with each addition, until two molecular proportions of the potassium salt have been added, *i.e.*, until the neutral salt of the bibasic chelidonic acid has been formed. Further addition of potash produces a permanent yellow coloration, but the solution does not remain alkaline until more than three molecular proportions of potassium hydroxide have been added. This yellow solution contains the potassium salt of a new acid, *xanthochelidonic acid*. If this solution is acidified with acetic acid, it gives a yellow precipitate,  $\text{C}_7\text{H}_2\text{Pb}_2\text{O}_7 + \text{H}_2\text{O}$ , with lead acetate; tetrabasic calcium and silver salts could not be prepared. By acidifying a solution of chelidonic acid in excess of caustic potash with nitric acid, a light yellow crystalline deposit of an acid potassium salt,  $\text{C}_7\text{H}_5\text{KO}_7$ , was obtained. The free acid cannot be isolated from its salts, since by the addition of an acid it is at once partly converted into chelidonic acid, and still more so on standing.

If chelidonic acid is treated with hydriodic acid, it yields pimelic acid (probably the normal acid). When it is heated with zinc and acetic acid, and the zinc removed by sulphuretted hydrogen, an acid, *hydrochelidonic acid*,  $\text{C}_7\text{H}_{10}\text{O}_5$ , is obtained. This is colourless, crystalline, melts at  $142^\circ$ , and can be distilled unchanged. The zinc salt,  $\text{C}_7\text{H}_8\text{O}_5\text{Zn} + 2\text{H}_2\text{O}$ , is but slightly soluble in cold water, and crystallises in small monoclinic tables,

$$a : b : c = 1.0292 : 1 : 1.737; \beta = 80^\circ 7.5'; \text{OP} \cdot \infty \text{P}\infty \cdot \infty \text{P}2.$$

also —  $\text{P}\infty \cdot \text{P}\infty \cdot \text{P}2$ .

The calcium salt,  $\text{C}_7\text{H}_8\text{O}_5\text{Ca} + \text{H}_2\text{O}$ , is indistinctly crystalline. The silver salt is  $\text{C}_7\text{H}_5\text{O}_5\text{Ag}_2$ ; the copper, lead, and mercurous salts are also mentioned.

An alkaline solution of hydrochelidonic acid was treated with potassium permanganate, and oxalic and succinic acids obtained, in

accordance with the equation  $C_7H_{10}O_5 + 6O = C_2O_4H_2 + C_4H_6O_4 + CO_2 + H_2O$ .

Hydrochelidonic acid heated with a saturated solution of hydriodic acid at 200—210° is in greatest part reduced to *pimelic acid*,  $C_7H_{12}O_4$ , which is obtained by simple evaporation; it melts at 102·9—103·9°, and forms monoclinic crystals,

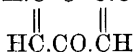
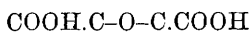
$$a : b : c = 3\cdot691 : 1 : 2\cdot058; \beta = 103^\circ 33'; \infty P \infty . OP . \infty P . P .$$

It is probably the normal acid. During the reduction, a small quantity of a hydrocarbon is also formed.

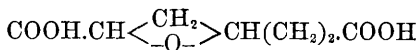
An alkaline solution of sodium xanthochelidonate was reduced with sodium amalgam, and the new sodium salt precipitated from the concentrated solution by alcohol. The silver salt was found to have the formula  $Ag_2C_7H_{10}O_7$ , hence *hydroxanthochelidonic acid* must have the composition  $C_7H_{12}O_7$ ; it is a syrupy liquid. Heated with hydriodic acid, it also acts like hydrochelidonic acid and chelidonic acid.

If chelidonic acid is heated at 240° it loses 2 mols.  $CO_2$ , and gives as distillate a body melting at 32·5°, and boiling at 215°. With aqueous ammonia it gives hydroxypyridine (*Monatsh. Chem.*, 1883, 339), and there is no doubt that it is identical with Ost's pyrocomene (*J. pr. Chem.*, 29, 63), thus showing a connection between chelidonic and meconic acids.

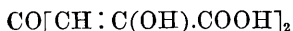
Chelidonic acid is certainly dibasic; the pimelic acid referred to is probably the normal acid, and by boiling with an alkali chelidonic acid yields oxalic acid and acetone. These and other facts are explained by the constitutional formulæ:—



Chelidonic acid.



Hydrochelidonic acid.



Xanthochelidonic acid.

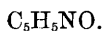


Hydroxanthochelidonic acid.

H. B.

**Nitrogenous Derivatives of Meconic Acid.** By H. OST (*J. pr. Chem.* [2], 29, 57—69).—In previous papers (Abstr., 1879, 708, and 1883, 791), the author has described those nitrogenous compounds which are readily obtainable from meconic acid, as substituted products of a hypothetical pyridone:—

Pyridone,



Pyromecazonic acid,  $C_5H_3NO(OH)_2$ .

Comenamic acid,  $C_5H_3NO(OH)(COOH)$ .

The author now shows that pyridone is hydroxypyridine, that pyromecazonic acid is a trihydroxypyridine, and comenamic acid a dihydroxypyridinecarboxylic acid.

*Ethyl diacetylcomenamate*,  $C_5H_2N(OAc)_2.COOEt$ , was prepared by boiling ethyl comenamate with excess of acetic anhydride and then evaporating. The diacetyl-compound melts at 38°, whilst the

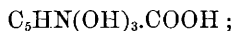
monacetyl-derivative, which is formed when the above mixture is only warmed, melts at  $152^{\circ}$ . Both compounds are decomposed by water or alcohol in the cold, with liberation of acetic acid.

The *ethyl dibenzoylcomenamate*, which is obtained by boiling ethyl comenamate with benzoic chloride, melts at  $102^{\circ}$ , and is more stable than the acetyl-compounds.

Since the existence of these diacetyl- and dibenzoyl-compounds does not conclusively prove that comenamic acid contains two hydroxyl and not one hydroxyl and one imido-group, the isolation of pyridone was next proceeded with and accomplished by means of the acid  $C_6H_2Cl_2O_2$ , to which the author gives the name of dichlorocomanic acid, comanic acid,  $C_6H_3O_2.COOH$ , being comenic acid in which the hydroxyl is replaced by hydrogen.

*Dichlorocomanic acid*,  $C_6HCl_2O_2.COOH$ , is prepared by heating comenic acid with 4 mols. of phosphorus pentachloride and oxhydrochloride, using a reflux condenser, until no more hydrochloric acid is evolved; on then distilling to  $150^{\circ}$  an oil remains behind which yields the acid when decomposed with warm water. When purified, by crystallisation from alcohol, the acid forms voluminous needles melting at  $217^{\circ}$ . A small quantity of monochlorocomanic acid is formed at the same time; this crystallises in needles, and melts at  $247^{\circ}$ .

*Comanic acid*,  $C_6H_3O_2.COOH$ , is obtained by boiling the dichlorinated acid for several hours with rather more than the theoretical proportion of aqueous hydriodic acid (b. p.  $127^{\circ}$ ); the iodine is then driven off in a current of steam, and on evaporating the solution the acid crystallises out in small nodules. The pure acid forms small oblique prisms melting at  $250^{\circ}$  with violent evolution of gas. It gives no coloration with ferric chloride. The barium, silver, and ethyl salts are described; the latter melts at  $103^{\circ}$ , and is not acted on by acetic anhydride or chloride. This shows that comanic acid is not a hydroxy acid, although barium hydroxide precipitates a basic salt, which, however, is derived from another acid into which comanic acid is readily converted by strong bases, and which gives a dark brown-red coloration with ferric chloride. On heating it with excess of barium hydroxide, the precipitate formed is rapidly converted into barium oxalate, acetone being formed also; in this respect, comanic resembles chelidonic acid (Abstr., 1883, 870). When comanic acid is heated, carbonic anhydride is evolved, and it is converted into pyrocomane,  $C_5H_4O_2$ , a neutral body soluble in water, melting at  $32^{\circ}$ , and boiling at  $210-215^{\circ}$ . On gently heating comanic acid with strong ammonia, it is readily converted into  $\beta$ -hydroxypicolinic acid,  $C_5H_3N(OH).COOH$ , which has already been described (Abstr., 1883, 791). Since this acid can also be obtained from pentachloropicoline, there is no doubt that it is hydroxypyridinecarboxylic acid. In a similar manner, although less readily, ammonia acts on comenic acid, yielding comenamic acid,  $C_6H_2N(OH)_2.COOH$ , and on hydroxycomenic acid, yielding hydroxycomenamic acid,



this proves that comenamic acid is a dihydroxy-, and hydroxy-

comenamic acid a trihydroxy-pyridinecarboxylic acid; both these acids, moreover, belong to the  $\alpha$ -pyridinecarboxylic series.

*Hydroxypyridine*,  $C_5H_4N.OH$ , is obtained from  $\beta$ -hydroxypicolinic acid by heating it above its melting point, carbonic anhydride being evolved. It crystallises in small grains melting at  $148^\circ$ , is easily soluble in water and alcohol, has a neutral reaction, combines with acids, and forms a platinochloride crystallising in large rectangular prisms. This hydroxypyridine is identical with that obtained by Lieben and Haitinger (Abstr., 1883, 870). The following is a list of the nitrogenous derivatives of meconic acid:—

*Hydroxypyridines.*

$C_5H_4NOH$ , hydroxypyridine.

$C_5H_3N(OH)_2$ , dihydroxypyridine, pyrocomenamic acid.

$C_5H_2N(OH)_3$ , trihydroxypyridine, pyromecazonic acid.

$C_5H_2NO_2.OH$ , hydroxypyridinequinone, pyromecazone.

$C_5HN(OH)_4$ , tetrahydroxypyridine (?), hydroxypyromecazonic acid.

$C_5H_2NMe(OH)_2$ , dihydroxypicoline, methyl dihydroxypyridone (Abstr., this vol., p. 840).

*Hydroxypyridinecarboxylic Acids.*

$C_5N_3N(OH).COOH$ ,  $\beta$ -hydroxypicolinic acid (and the isomeric  $\alpha$ - and  $\gamma$ -acids).

$C_5H_2N(OH)_2.COOH$ , dihydroxypicolinic acid, comenamic acid.

$C_5HN(OH)_3.COOH$ , trihydroxypicolinic acid, hydroxycomenamic acid.

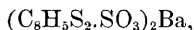
$C_5HNO_2(OH).COOH$ , hydroxypicolinic acid quinone, azonecarboxylic acid. P. F. F.

**Betaine in Cotton Seed.** By H. RITTHAUSEN and F. WEGER (*J. pr. Chem.*, **30**, 32—37).—The authors have succeeded in obtaining betaine from the cotton seed, by treatment of the mother-liquors from which melitose had been separated (*J. pr. Chem.*, **29**, 351). The authors have not as yet determined in what form the betaine occurs in the cotton seed. P. P. B.

**Seleniocarbamide.** By A. VERNEUIL (*Bull. Soc. Chem.*, **41**, 599).—This compound may be prepared by the action of hydrogen selenide on cyanamide. The latter dissolved in ether absorbs the gas completely in the cold, and after a short time crystals are deposited and finally the liquid becomes solid. The reaction is facilitated by the presence of a small quantity of ammonia. The compound purified by two crystallisations from boiling water forms white crystals which assume a rose tint when exposed to light. Seleniocarbamide is very soluble in hot water, less so in cold, which dissolves 10.7 per cent. at  $19^\circ$ . Absolute alcohol dissolves 28 per cent. at  $18^\circ$ , and ether 0.56 per cent. at the same temperature. When rapidly heated, the compound melts without any apparent decomposition, but if slowly heated it melts at about  $200^\circ$  with decomposition. W. R. D.

**The Thiophene Group.** By R. NAHNSEN (*Ber.*, **17**, 2197—2198).—The author has prepared larger quantities of dithienyl (Abstr.,

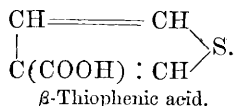
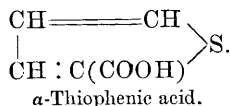
1884, 1132), and has submitted it to a more thorough examination than was previously possible. It crystallises from hot alcohol or glacial acetic acid in silky scales, melts at  $83^{\circ}$ , and boils at  $266^{\circ}$ . Its solution in concentrated sulphuric acid is reddish-brown in transmitted and deep-green by reflected light, and in pouring the solution into water dithienyl separates unchanged. *Dithienylsulphonic acid*,  $C_8H_5S_2SO_3H$ , is obtained by heating dithienyl with 20 times its weight of sulphuric acid. The barium salt



is obtained as a crystalline mass and is hygroscopic; the *potassium salt* is deliquescent and yields dithienyl when distilled with ammonium chloride. *Perbromodithienyl*,  $C_8Br_6S_2$ , is prepared by heating a solution of dithienyl in glacial acetic acid with an excess of bromine. It is very sparingly soluble in hot alcohol and in cold benzene, readily in boiling benzene, from which it crystallises in small needles melting at  $255^{\circ}$  (uncorr.).

A. K. M.

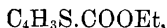
**$\beta$ -Thiophenic Acid.** By R. NAHNSEN (*Ber.*, 17, 2192—2196).—A thiophenic acid was prepared by Meyer and Kreis from thiophenesulphonic acid by Merz's method (*Abstr.*, 1884, 46). In the hopes of obtaining larger quantities of this acid, the author submitted a mixture of iodothiophene and ethyl chlorocarbonate to the action of sodium amalgam. The reaction takes place much more readily than in the case of Wurtz's synthesis of benzoic acid. The product is steam-distilled, the distillate extracted with ether, and the oil obtained is boiled for five hours with concentrated aqueous potash: the solution is diluted, separated from the unattacked iodothiophene, supersaturated with sulphuric acid, and extracted with ether. The thiophenic acid,  $C_4H_3S.COOH$ , obtained is, however, isomeric with that obtained by Meyer and Kreis, and melts constantly at  $129^{\circ}$ . The acid prepared from the sulphonate is assumed to be an  $\alpha$ -derivative, in which case the new acid would be  $\beta$ -thiophenic acid, thus:



$\beta$ -Thiophenic acid closely resembles benzoic acid. It crystallises in colourless needles, can be sublimed, and distils at  $260^{\circ}$ ; it yields a blue solution when heated with sulphuric acid and isatin. It gives white precipitates with silver nitrate, lead acetate, and mercurous nitrate, and a very bulky yellow precipitate with ferric chloride; whilst copper, cadmium, zinc, ferrous, cobalt, nickel, mercuric, barium, calcium, and magnesium salts produce no precipitate. The *silver salt*,  $C_4H_3S.COOAg$ , forms lustrous transparent scales or needles somewhat soluble in hot, sparingly in cold water; the *calcium salt*,  $(C_4H_3S.COO)_2Ca.3H_2O$ , is readily soluble in water, and separates in clusters of lanceolate crystals; the *barium salt*,



forms small lustrous crystals readily soluble in water. The *chloride*,  $C_4H_3S.COCl$ , is a colourless liquid boiling at  $190^\circ$  (uncorr.), and has the same penetrating odour as benzoic chloride; the *ethyl salt*,



is a colourless, strongly refracting liquid, boils at  $218^\circ$  (corr.), and has an odour closely resembling that of ethyl benzoate.  $\beta$ -Thiophenamide,  $C_4H_3S.CONH_2$ , forms dense prisms melting at  $180^\circ$  (uncorr.). When  $\beta$ -thiophenic acid is nitrated and the product crystallised from water, dense yellow prisms,  $C_4H_2S(NO_2).COOH$ , first crystallise out, and afterwards long needles.

A. K. M.

**Action of Chlorine on Boiling Benzene.** By R. SCHÜPPHAUS (*Ber.*, **17**, 2256—2260).—Meunier (*Abstr.*, 1884, 733) has described a compound obtained in the preparation of benzene hexachloride, and has ascribed the formula  $\alpha C_6H_6Cl_6$  to it. The author also discovered this substance independently about two years ago. Meunier noticed the presence of this substance *after* sublimation of his crude product, and it has been thought it might have been formed at the high temperature of sublimation. The author obtained it, however, amongst the first crude crystals deposited after the action of the chlorine on the benzene. From the results of his analysis, and the general character of the compound, the author believes the formula of this compound to be  $C_{12}H_{10}Cl_{12}$ , and not  $\alpha C_6H_6Cl_6$ , and that it is thus *diphenyl dodecachloride*.

The crystals are brittle and become highly electrified when powdered in a mortar. Contrary to the statements of Meunier, the crystals are strongly double refracting. They belong to the regular system.

L. T. T.

**Isomeride of Benzene Hexachloride.** By J. MEUNIER (*Bull. Soc. Chim.*, **41**, 530—532).—The vapour-density of this compound, the preparation and properties of which have previously been described (*Abstr.*, 1884, 733), has been determined, and found to be 9.365 and 9.207 at  $260^\circ$  (theor. 10.03). The vapour-density of ordinary benzene hexachloride at  $220^\circ$  was found to be 10.139. This difference is probably due to partial decomposition of the isomeride at the temperature of the determination. The formula of this isomeride is therefore  $C_6H_6Cl_6$ , and its melting point is about  $310^\circ$ , that of ordinary benzene hexachloride being  $157^\circ$ .

A. B.

**Orthonitrobenzyl Chloride.** By E. NÖLTING (*Bull. Soc. Chim.*, **41**, 502—504).—Since the oil obtained as a bye-product in the preparation of paranitrobenzyl chloride (*Abstr.*, 1884, 1005) consists chiefly of orthonitrobenzyl chloride, it may, perhaps, serve as a means of preparing orthonitrobenzaldehyde, the starting point in Baeyer's synthetical preparation of indigo, but the author has not yet succeeded in preparing the aldehyde from the oil.

A. B.

**Decomposition of Benzonitrile by Fuming Sulphuric Acid.** By F. GUMPERT (*J. pr. Chem.*, **30**, 87—90).—In preparing *cyaphenine* according to Pinner and Klein's method (*Abstr.*, 1878, 864), the

author did not obtain this compound, but *dibenzamide*,  $\text{NHBz}_2$ , identical with that prepared by Barth and Senhofer (*Ber.*, **9**, 975), and by Fischer and Troschke (*Abstr.*, 1881, 51). Dibenzamide melts at  $148^\circ$ . When heated with alkalis, it is converted into benzoic acid and ammonia; heated with alcoholic ammonia in sealed tubes, it is converted into benzamide. The compound described by Pinner and Klein as *dibenzimide oxide* is formed along with the above compound; when treated with dilute hydrochloric acid it is converted into dibenzamide, and the author regards it as benzimidobenzamide,  $\text{NHBz.CPh:NH}$ .

P. P. B.

**Acetonequinol.** By S. HABERMANN (*Monatsh. Chem.*, **5**, 329—331).—Quinol dissolves easily in acetone and, on cooling, very fine crystals of *acetonequinol*,  $\text{C}_3\text{H}_6\text{O.C}_6\text{H}_6\text{O}_2$ , separate out. When exposed to the air, they soon become opaque, and then consist only of quinol. In composition and easy decomposition, it resembles quinhydrone, and its existence is an argument in favour of the formula for quinone, recently advocated by Kekulé (*Annalen*, **223**, 170), showing two carbonyl-groups.

H. B.

**New Synthesis of Saligenin.** By W. H. GREENE (*Chem. News*, **50**, 76).—A mixture of methylene chloride (30 grams), phenol (30 grams), sodium hydroxide (40 grams), and water (50 grams), is heated in a sealed tube at  $100^\circ$  for six hours; the contents of the tube are then neutralised with hydrochloric acid, extracted with ether, and the ether distilled off. The residue is repeatedly treated with boiling water, the aqueous solution is concentrated, the drops of phenol which separate are removed, and the strong solution then left to crystallise over sulphuric acid; the product, when recrystallised from boiling water, is pure *saligenin*.

D. A. L.

**Compounds of Glucoses and Sucroses with Phenylhydrazine.** By E. FISCHER (*Ber.*, **17**, 579—584).—When an aqueous solution of phenylhydrazine hydrochloride, to which sodium acetate has been added, is heated on the water-bath with the aqueous solution of a sugar, combination takes place and an insoluble compound is formed. In many cases, the production of these compounds may be used as a means of detecting the presence of a sugar and of identifying the same. They may, as a rule, be easily purified by crystallisation from alcohol. Of the sugars experimented with, inosite and trehalose are the only two which have not the property of uniting with phenylhydrazine.

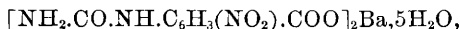
*Phenylglucosazone*,  $\text{C}_{18}\text{H}_{22}\text{N}_4\text{O}_4$ , is the name given by the author to the compound formed when dextrose or levulose is treated with phenylhydrazine in the manner described. This compound is insoluble in water, but soluble in boiling alcohol, from which it is precipitated by water in slender yellow needles melting at  $204\text{--}205^\circ$ . It is not acted on by aqueous solutions of caustic alkalis, but is decomposed by strong hydrochloric or sulphuric acids, with the production of dark red solutions. This compound is formed even when dilute solutions of dextrose are employed, and it would appear that its production may be used as a means of detecting grape-sugar in urine.



*Phenylgalactosazone*,  $C_{18}H_{22}N_4O_4$ , is the product of the combination of phenylhydrazine and galactose; in properties, it resembles phenylglucosazone, differing from it in melting at a lower temperature, namely,  $182^\circ$ .

Sorbin also unites with phenylhydrazine, forming a compound which is easily soluble in hot alcohol, and may be precipitated from the solution by water, in the form of fine yellow needles melting at  $164^\circ$ . When cane-sugar is warmed with the solution of phenylhydrazine hydrochloride, it is first inverted, and subsequently phenylglucosazone is produced. Milk-sugar and maltose both unite with phenylhydrazine, forming *phenylactosazone* and *phenylmaltosazone* respectively. These compounds have the same composition, viz.,  $C_{24}H_{32}N_4O_9$ , are soluble in hot water, and crystallise in yellow needles; the former melts at  $200^\circ$ , the latter at  $190-191^\circ$ .  
P. P. B.

**Action of Potassium Cyanate on Metanitramidobenzoic Acid.** By P. GRIESS (*Ber.*, 17, 2184—2187).—Five isomeric uramido-nitrobenzoic acids have been described, in three of which the groups  $NO_2$  and  $NH.CO.NH_2$  occupy the ortho-position to one another, and in the remaining two, the para-position. With the object of obtaining an acid containing these groups in the meta-position, the author has submitted metanitramidobenzoic acid (*Abstr.*, 1884, 314) to the action of potassium cyanate. The nitramidobenzoic acid is gradually added to a cold aqueous solution of crude potassium cyanate, the mixture heated for some hours at  $50-60^\circ$ , and then treated with an excess of acetic acid. The product is allowed to stand for several hours, a large excess of hydrochloric acid is added, and the precipitate separated and washed. The product consists of two acids: *uramidonitrobenzoic acid*,  $NH_2.CO.NH.C_6H_3(NO_2).COOH$  [1 : 3 : 5], and *diuramidonitrobenzoic acid*,  $(NH_2.CO)_2N.C_6H_3(NO_2).COOH$  [1 : 3 : 5], which may be separated either by treatment with boiling water or by means of the barium salts. Uramidonitrobenzoic acid,  $C_6H_3N_3O_5.H_2O$ , is moderately soluble in boiling water, from which it crystallises in bright yellow needles; is much more readily soluble in hot alcohol, but very sparingly in ether; it has a strong bitter taste. When heated, it detonates, producing a yellow smoke and leaving a large carbonaceous residue. The *barium salt*,



forms yellow nodules, readily soluble in hot, moderately in cold water. On dissolving uramidonitrobenzoic acid in nitric acid (sp. gr. 1.5), it is converted into uramidodinitrobenzoic acid,



Diuramidonitrobenzoic acid crystallises from alcohol with 2 mols.  $H_2O$ . It forms almost white microscopic needles or scales generally united in tufts, is very sparingly soluble even in boiling water, and sparingly also in hot alcohol and in ether. It has a strong bitter taste, and also resembles the last acid in its behaviour when heated. By the action of tin and hydrochloric acid, it is converted into a new amido-acid, crystallising from boiling water in slender white needles.

The *barium salt*,  $[(\text{NH}_2\text{CO})_2\text{N.C}_6\text{H}_3(\text{NO}_2).\text{COO}]_2\text{Ba}, 7\frac{1}{2}\text{H}_2\text{O}$ , is very sparingly soluble even in boiling water, and crystallises from it in small yellow nodules when the solution is rapidly cooled, and in needles by slow crystallisation; it is insoluble in alcohol. A. K. M.

**Action of Hydrochloric Acid and of Chlorine on Acetobenzonic Anhydride.** By W. H. GREENE (*Chem. News*, 50, 61—62).—It has been stated (Loir, *Abstr.*, 1880, 31) that acetobenzonic anhydride prepared from benzoic chloride and sodium acetate, differs from the anhydride prepared from acetic chloride and sodium benzoate in its reactions with hydrochloric acid and with chlorine. The author shows that this is not the case, but that acetobenzonic anhydride, whichever way prepared, behaves always in the same manner with hydrochloric acid and chlorine. When dry hydrochloric acid is passed into the anhydride at ordinary temperatures, acetic chloride and benzoic acid are the principal products, whilst at higher temperatures,  $130^\circ$  to  $150^\circ$ , acetic and benzoic chlorides, and acetic and benzoic acids, are produced in about equivalent proportions. With chlorine at about  $150^\circ$ , the products are acetic and benzoic chlorides, chloroacetic and (1 : 2) chlorobenzoic acids, whilst at lower temperatures the reaction yields chiefly acetic chloride and chlorobenzoic acid. D. A. L.

**Action of Phenol and Sulphuric Acid on Hippuric Acid.** By J. ZEHENTER (*Monatsh. Chem.*, 5, 332—338).—Experiments were made to obtain condensation-products of phenol with glycocholic acid and alanine, but with negative results. But by heating hippuric acid with phenol and sulphuric acid at  $140^\circ$ , the nascent glycocholic acid unites completely with the phenol. The product of the reaction is dissolved in water, the benzoic acid removed by ether, and then neutralised while hot with lead carbonate. The solution of the lead salt is decomposed with sulphuretted hydrogen, and the filtrate evaporated finally in a vacuum and allowed to crystallise. The substance,  $\text{C}_8\text{H}_9\text{O}_5\text{NS} + \text{H}_2\text{O}$ , melts at  $183$ — $185^\circ$ , and is an acid forming salts. It is probably *sulphophenylglycocholic*, its formation being expressed by the equation  $\text{NH}_2\text{CH}_2\text{COOH} + \text{C}_6\text{H}_5\text{OH} + \text{H}_2\text{SO}_4 = \text{C}_8\text{H}_9\text{O}_5\text{NS} + 2\text{H}_2\text{O}$ . The *silver salt*,  $\text{C}_8\text{H}_9\text{O}_5\text{NSAg} + 3\text{H}_2\text{O}$ , the *barium salt*,  $(\text{C}_8\text{H}_9\text{O}_5\text{NS})_2\text{Ba} + \text{H}_2\text{O}$ , and also the copper and potassium salts are described.

When the free acid is heated to  $200^\circ$ , it gives a distillate of phenol. Treated with aqua regia, a yellow crystalline substance is formed. No satisfactory clue to the constitution of the acid is obtained by fusing it with alkalis. Phenol and hippuric acid do not act on each other if heated with water under pressure. H. B.

**Nitrocumenylacrylic Acids and their Derivatives.** By O. WIDMANN (*Ber.*, 17, 2282—2284).—As Einhorn and Hess have just published a communication containing some work on this subject, the author now gives a preliminary note of the results of a research which he has been carrying on of late. He has at present prepared and examined the following compounds:—

## A. From orthonitrocumenylacrylic acid—

Ethyl orthonitrocumenylacrylate . . . . .	Liquid.
Orthonitrocumenylacrylic acid dibromide..	m.p. 171°
Orthamidocumenylacrylic acid . . . . .	„ 165
Acetamidocumenylacrylic acid . . . . .	„ 220
Cumostyryl (isopropylcarbostyryl) . . . . .	„ 167—168
Hydrocumostyryl . . . . .	„ 135
Orthoxycumenylacrylic acid . . . . .	„ 176

## B. From cumenylnitroacrylic acid—

Cumenylamidoacrylic acid . . . . .	„ 154—155
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## C. From metanitrocumenylacrylic acid—

Metanitrocumenylacrylic acid. . . . .	„ 141
Ethyl metanitrocumenylacrylate . . . . .	„ 58—59
Metanitrocumenylacrylic acid dibromide ..	„ 184
Metamidocumenylacrylic acid . . . . .	„ 165
Acetamidocumenylacrylic acid . . . . .	„ 240
Metamidocumenylpropionic acid . . . . .	„ 103—105
Acetamidocumenylpropionic acid . . . . .	„ 168
	L. T. T.

**Compounds of Phenols with Ethyl Acetoacetate.** III. By H. v. PECHMANN and J. B. COHEN (*Ber.* 17, 2187—2191). In continuation of their experiments on the substituted coumarins (*Abstr.*, 1884, 66, 1331) the authors give further evidence of the general application of the reaction for their formation. A comparison of the coumarins obtained from ethyl acetoacetate with the ordinary coumarins shows a striking analogy in the properties and especially in the colour reactions of those members of both series which are derived from the same phenol.

The coumarin obtained from paracresol and ethyl acetoacetate (*loc. cit.*) may (in accordance with Baeyer's notation, *Abstr.*, 1884, 998) be named  $\beta$ -5-dimethylcoumarin; it melts at 148°.

$\beta$ -Methyl $\alpha$ -daphnetin,  $C_6H_2(OH)_2 < \frac{CMe:CH}{O} > CO$  [1 : 2 : 3 : 4], obtained from pyrogallol and ethyl acetoacetate (*loc. cit.*), closely resembles daphnetin; after boiling with bisulphite, both compounds yield an intense blue coloration with ferric chloride and a reddish-yellow reaction with ammonia and potassium ferricyanide. The action of sulphuric acid on orcinol and ethyl acetoacetate has been examined by Wittenberg (*J. pr. Chem.* [2], 26, 69), but his results disagree with the authors'. The product is termed  $\beta$ -6-dimethylumbelliferone,  $C_6H_2Me(OH) < \frac{CMe:CH}{O} > CO$  [ $CMe : O : OH : Me = 1 : 2 : 4 : 6$ ]. It melts at 248—250°, crystallises in needles, dissolves readily in alcohol and glacial acetic acid, sparingly in benzene and chloroform, and is almost insoluble in water. It yields yellow solutions with concentrated sulphuric acid and with dilute alkalis. The solution obtained by boiling it with bisulphite yields (like homo-umbelliferone) a red coloration. The *acetyl-derivative*,  $C_{13}H_{12}O_4$ , crystallises in white needles,

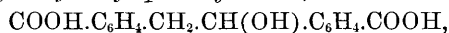
melting at  $195^{\circ}$ , dissolves readily in alcohol, glacial acetic acid, benzene, and chloroform, sparingly in ether, and is insoluble in water. 4-6-Dihydroxy- $\beta$ -methylcoumarin,



from phloroglucol and ethyl acetoacetate is isomeric with  $\beta$ -methyl-daphnetin. It crystallises in colourless needles, melts at  $282\text{--}284^{\circ}$ , dissolves readily in alcohol and glacial acetic acid, sparingly in water, benzene, and chloroform, is almost insoluble in ether, and is readily dissolved by dilute alkalis. Its aqueous solution gives no reaction with ferric chloride, and yields a yellow precipitate with lead acetate. It yields no colour reaction with bisulphite. The *acetyl-derivative*,  $\text{C}_{14}\text{H}_{12}\text{O}_6$ , crystallises from alcohol in white glistening needles, melts at  $138\text{--}140^{\circ}$ , is insoluble in water, sparingly soluble in ether, readily in alcohol, glacial acetic acid, and chloroform.  $\beta$ -Methylcoumarin of naphthalene,  $\text{C}_{10}\text{H}_6 < \text{CMe} : \text{CH} \text{---} \text{O} \text{---} > \text{CO}$ , from  $\beta$ -naphthol and ethyl acetoacetate, forms white glistening needles, melting at  $161\text{--}162^{\circ}$ ; it dissolves in alcohol, benzene, and chloroform, but is nearly insoluble in water and ether. Sulphuric acid dissolves it with green fluorescence.

A. K. M.

**Reduction of Phthalic Anhydride by Zinc and Glacial Acetic Acid.** By J. WISLICENUS (*Ber.*, 17, 2178—2183).—When phthalic anhydride (200 grams) is dissolved in glacial acetic acid (1 kilo.), heated on a water-bath, and zinc-dust (about 300 grams) added in small quantities at a time, the latter at first dissolves rapidly, with considerable evolution of heat but without generating hydrogen; when the reaction becomes sluggish, heat is applied, and hydrogen is then seen to escape. The hot filtered solution deposits needles of *diphthaly*,  $\text{C}_{16}\text{H}_8\text{O}_4$ , on cooling; this melts above  $320^{\circ}$  and can be sublimed in a current of carbonic anhydride. On diluting the mother-liquor with water, a flocculent precipitate is obtained, containing *hydrodiphthaly*,  $\text{C}_{16}\text{H}_{10}\text{O}_4$ , and *hydrodiphthallactonic acid*,  $\text{C}_{16}\text{H}_{12}\text{O}_4$ , separable by means of sodium carbonate solution. Hydrodiphthallyl,  $\text{CO} < \text{C}_6\text{H}_4 \text{---} \text{O} \text{---} > \text{CH} \cdot \text{CH} < \text{C}_6\text{H}_4 \text{---} \text{O} \text{---} > \text{CO}$ , crystallises from boiling alcohol in slender colourless needles, melting between  $228^{\circ}$  and  $229^{\circ}$ ; it dissolves extremely readily in boiling glacial acetic acid. Hydrodiphthallactonic acid,  $\text{CO} < \text{C}_6\text{H}_4 \text{---} \text{O} \text{---} > \text{CH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , dissolves very readily in hot, sparingly in cold alcohol, and crystallises in short thick four-sided, vitreous prisms, melting at  $198.5^{\circ}$ ; the potassium salt is readily soluble, the silver salt,  $\text{C}_{16}\text{H}_{11}\text{O}_4\text{Ag}$ , forms a white very stable precipitate. On boiling the acid with excess of potash, two molecules of the latter become neutralised, and on then acidifying with hydrochloric acid, *hydrohydroxydiphthalylic acid*,



is obtained, crystallising in colourless prisms; this melts at  $170^{\circ}$  with separation of water, then solidifies and melts again at  $198.5^{\circ}$ . When hydrodiphthallactonic acid is boiled with hydriodic acid and phosphorus,

the acid,  $C_{16}H_{14}O_4$ , obtained by Graebe from diphthalyl, is formed, and is named by the author *dibenzylldiorthocarboxylic acid*,



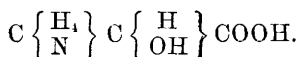
The diluted mother-liquor from the diphthalyl and diphthallactonic acid contains *phthalide* which can be separated by extraction with ether; it crystallises from warm ether and alcohol in dense strongly refracting prisms, and from boiling water in needles; it melts at  $73^\circ$ , and is volatile without decomposition, its boiling point being  $281.5^\circ$  at a pressure of 750 mm. ( $286.5^\circ$  corr.). The residual solution freed from phthalide still contains zinc salts of acetic, phthalic, and hydrodiphthallactonic acids.

The formation of diphthalyl from phthalic anhydride and zinc takes place thus:  $4C_8H_4O_3 + 2Zn = 2C_8H_4O_4Zn + C_{16}H_8O_4$ , this being proved by heating fused phthalic anhydride at  $130-140^\circ$  with zinc-dust (free from oxide), when a mixture of zinc phthalate and diphthalyl is obtained.

A. K. M.

**Isatin.** (Preliminary Note.) By H. KOLBE (*J. pr. Chem.*, **30**, 84—87).—Isatin is converted by chromic acid, dissolved in glacial acetic acid, into an acid which the author styles *isatoic acid*, and which he regards as *nitrogen-benzoylcarboxylic acid*,  $C_6\left\{\begin{smallmatrix} H \\ N \end{smallmatrix}\right\}CO.COOH$ .

It is sparingly soluble in cold water and alcohol, but easily in hot water, from which it crystallises in yellow rhombic tables. This same acid is obtained by oxidising indigo with chromic acid. When isatoic acid is heated above its melting point, or when its aqueous solution is boiled, it is decomposed, water and carbonic anhydride being formed. When boiled with baryta-water, a new acid is produced, which is easily soluble in water, and seems to be formed when isatoic acid is heated with sulphuric acid. In attempting to prepare the ethyl salt of this acid, a liquid was obtained, probably  $C_6H_4N.CO.OEt$ , and an acid, which is probably



P. P. B.

**Formation of Dibenzyl from Ethylene Dichloride and Benzene in Presence of Aluminium Chloride.** By W. H. GREENE (*Chem. News*, **50**, 61).—By applying Friedel and Crafts' reaction to a mixture of benzene and ethylene dichloride, the author has obtained *dibenzyl* (boiling point, according to present determination,  $279^\circ$  at 767 mm.), in nearly theoretical quantities, along with oily condensation-products, which can neither be completely distilled, even at  $200^\circ$  in a vacuum, nor fractioned, nor solidified in a freezing mixture.

D. A. L.

**Trichlorocamphor.** By P. CAZENEUVE (*Compt. rend.*, **99**, 609—611).—Monochlorocamphor (melting at  $83-84^\circ$ ) is heated on a water-bath and saturated with chlorine gas. The product is washed repeatedly with water in order to remove hydrochloric acid, then dissolved in alcohol, and the solution placed in a mixture of ice and

salt, when it separates into two layers, the lower of which is a molecular combination of the trichlorocamphor with alcohol, solidifying below  $0^{\circ}$ . This compound is decomposed by water, the product compressed in order to expel a liquid substance, which is in all probability a more highly chlorinated derivative, and then purified by repeated solution in alcohol and precipitation by water. The trichlorocamphor thus obtained has the composition  $C_{10}H_{13}Cl_3O$ , and forms white microscopic crystals, which have very little odour, and resemble terebenthene derivatives. It is insoluble in water, but dissolves easily in cold alcohol, ether, chloroform, carbon bisulphide, and the other solvents for camphor. It melts and solidifies at  $+54^{\circ}$ , liquefies in the vapours of ether and chloroform, like the mono- and di-derivatives, and in alcoholic solution has a dextrorotatory power  $[\alpha] = +64^{\circ}$ . When boiled, it decomposes with evolution of hydrochloric acid and formation of a carbonaceous residue.

From its appearance, solubilities, and crystalline form, this derivative seems to belong to the  $\beta$ -series of chlorocamphors.

C. H. B.

**Camphoronic Acid.** By J. KACHLER and F. V. SPITZER (*Monatsh. Chem.*, **5**, 415—416).—The formula  $C_9H_{12}O_5 \cdot H_2O$  has been previously given to this acid (*Annalen*, **159**, 286), which Kissling (*Inaug. Diss.*, Würzburg, 1878) believes to be an anhydride, the true acid being  $C_9H_{14}O_6$ . The authors are studying the action of aqua regia and potassium permanganate on the acid.

H. B.

**Kinoïn in Malabar Kino.** By C. ETTL (*Ber.*, **17**, 2241—2244).—Krempler (*Vienna pharmaceutische Post*, **16**, 117) and A. Bergholz (*Inaug. Dissert.*, Dorpat, 1884) deny the presence of kinoïn in Malabar kino, and state that they have found protocathechuic acid therein. The author proves the methods employed by these investigators to be very faulty, and fully sustains the correctness of his own earlier investigations on this subject (*Abstr.*, 1879, 159).

L. T. T.

**Substances contained in Saffron.** By R. KAYSER (*Ber.*, **17**, 2228—2234).—Bouillon, Vogel, Quadrat, Rochleder and Mayer, and Weiss have at various times worked at this subject, but the information at present available is unsatisfactory. The author has therefore carefully investigated a sample of saffron from *Crocus electus*, *Gatin*.

*Essential Oil of Saffron.*—This was obtained from saffron by steam-distillation in a current of carbonic anhydride. It is an almost colourless mobile liquid, with an intense odour of saffron. When exposed to the air, it becomes oxidised and turns brown and syrupy. Analysis showed its composition to be  $C_{10}H_{16}$ , so that it belongs to the class of terpenes.

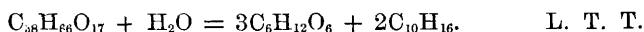
*Crocin.*—Saffron was first freed from fatty matters, &c., by ether and then extracted with water at the ordinary temperature. The aqueous solution was shaken up with bone-charcoal, which absorbed nearly all the colouring matter. The charcoal was filtered off, and the crocin extracted from it by washing with pure water. This solution was evaporated to dryness, and the residue treated with 90 per cent. alcohol. On evaporating the alcoholic solution, a yellowish-brown

brittle mass is left, which yields a yellow powder. Crocin is easily soluble in water and dilute alcohol, less so in absolute alcohol, and almost insoluble in ether. Strong sulphuric acid dissolves it to a deep blue solution, which turns first violet, then cherry-red, and lastly brown. Nitric acid (sp. gr. 1.4) gives a similarly coloured solution, but the colour immediately changes to brown. Hydrochloric acid yields a yellow solution. Lead acetate, and lime- and baryta-water give no precipitate, but, on heating, they decompose crocin into crocetin and a sugar. Alkalis cause the same decomposition in the cold. Crocin is thus a glucoside, and analysis shows its composition to be  $C_{41}H_{70}O_{28}$ .

*Crocetin* is best obtained by the action of hydrochloric acid on crocin. It is precipitated in the form of yellow flocks, which when dried yield a red powder. It is almost insoluble in pure water, but is rendered soluble by the addition of a small quantity of an alkali. Acids reprecipitate it from such solutions in orange flocks. It is easily soluble in alcohol. An alcoholic solution gives bright red precipitates with lead acetate, and with lime- or baryta-water; the compounds so formed, however, are not definite, but vary in composition. Sulphuric and hydrochloric acids behave with it as with crocin. Its composition is  $C_{34}H_{16}O_9$ . The decomposition appears to take place according to the equation  $2C_{44}H_{70}O_{28} + 7H_2O = C_{34}H_{16}O_9 + 9C_6H_{12}O_6$ .

*Crocose*.—The sugar mentioned above yields rhombic crystals. Its solution has a sweet taste and strong dextrorotatory action. Its reducing power for Fehling's solution is only half that of dextrose. The quantities of crocetin and crocose obtained by the decomposition agree very closely with those required by the above equation.

*Picrocrocetin*.—*Saffron-bitter*.—This substance crystallises out in the ether-extracting apparatus if the extraction be continued for a long time. It forms colourless prismatic needles, very sparingly soluble in ether. It dissolves easily in water and alcohol, less so in chloroform. It has a characteristic bitter taste, which is very persistent. It melts at  $75^\circ$  to a colourless liquid. Its formula is  $C_{38}H_{66}O_{17}$ . Lead acetate, lime-water, and baryta-water give no precipitate in the cold, but decomposition takes place on warming, crocose and the terpene described above being formed. Picrocrocetin is thus a glucoside like crocin, and the decomposition may be expressed by the equation—



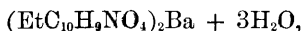
**Carboxylic Acids from Synthetically Prepared Pyridine Bases.** By R. MICHAEL (*Annalen*, 225, 121–146).—Hantzsch has recently described the synthesis of a pyridine-derivative, ethyl hydrocollidinecarboxylate, by the action of ethyl acetoacetate on aldehydammonia, the formation from it of collidinedicarboxylic acid, and further, the limited oxidation of this latter substance by which it is converted into lutidinetricarboxylic acid, picolinetetracarboxylic acid, and pyridinepentacarboxylic acid (*Abstr.*, 1883, 82). The present paper deals with the formation of a collidinemonocarboxylic acid and its oxidation into a series of acids each containing a COOH-group less than those above mentioned.

*Collidinemonocarboxylic acid* is formed by heating collidinedicarboxylic acid, but in such small quantity that a more satisfactory method for its preparation had to be found.

*Hydrogen ethyl collidinedicarboxylate*,  $C_5NMe_3(COOEt).COOH$ , is prepared by heating the diethyl salt with the quantity of alcoholic potash necessary to saponify only one  $COOEt$ -group; any undecomposed diethyl salt was then removed by shaking with ether, the solution of the potassium ethyl salt evaporated to dryness with the equivalent amount of hydrochloric acid, and the hydrogen ethyl salt separated from potassium chloride by solution in absolute alcohol. It crystallises ( $+2H_2O$ ) from water in rosettes of long prisms or in thick well-formed prisms, apparently of the monoclinic system; from alcohol in stellate groups of needles. It melts, when anhydrous, at  $157^\circ$ , is readily soluble in alcohol and water, sparingly soluble in ether. The following salts were prepared from it. The *acid silver salt*,



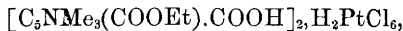
forms small monoclinic prisms, and is not blackened by exposure to light. The *zinc salt*,  $(EtC_{10}H_9NO_4)_2Zn + 5H_2O$ , crystallises in rosettes of colourless prisms, sparingly soluble in cold, readily in hot water. The *cadmium salt*,  $(EtC_{10}H_9NO_4)_2Cd + 4H_2O$ , crystallises in striated prisms, and is readily soluble in hot water. The *copper salt*,  $(EtC_{10}H_9NO_4)_2Cu$ , forms an indigo-blue powder consisting of microscopic plates. It is anhydrous and insoluble in water. The *calcium salt*,  $(EtC_{10}H_9NO_4)_2Ca + 3H_2O$ , forms crusts of fine needles, and is readily soluble in water and alcohol. The *barium salt*,



is sparingly soluble in water, insoluble in alcohol. It can also be obtained with only 1 mol.  $H_2O$ . The *potassium salt* crystallises with 1 mol.  $H_2O$  in fibrous masses. The *nickel salt* crystallises in pale green prisms, the *mercurous salt* in thick tables. The hydrogen ethyl salt, like the free acid, combines with acids: the *hydrochloride*,



prepared by the action of hydrochloric acid on an ethereal solution of the salt, crystallises in thick transparent cube-like forms, melts at  $178^\circ$  with decomposition, is very readily soluble in water, readily soluble in alcohol. The *platinochloride*,



crystallises in red rhombic (?) tables, or with 2 mols.  $H_2O$  in large, broad prisms, is sparingly soluble in cold alcohol, readily soluble in water; it melts with decomposition at  $219^\circ$ .

*Ethyl collidinemonocarboxylate*,  $C_5NHMe_3.COOEt$ , was obtained in very small quantity by Hantzsch (*loc. cit.*) by heating ethyl hydrocollidinemonocarboxylate with hydrochloric acid; it is readily obtained by heating hydrogen ethyl collidinedicarboxylate, when it passes over between  $250^\circ$  and  $260^\circ$ , and can be purified by continued fractionation. The yield is 56—58 per cent. of the theoretical. It is a colourless oil, distils at  $256^\circ$ , has a sp. gr. = 1.0315 at  $15^\circ$ , and is readily

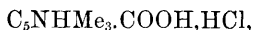


soluble in ether, alcohol, benzene, chloroform, and dilute acids. Crystalline compounds with acids could not be obtained. The *platinochloride*,  $(C_5NHMe_2.COOEt)_2.H_2PtCl_6$ , crystallises in thick reddish-yellow prisms, and melts at  $193^\circ$ ; it is sparingly soluble in alcohol, readily soluble in water. *Ethyl collidinecarboxylate methiodide*,

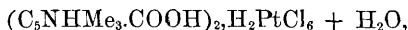


formed by the union of its components at ordinary temperatures, crystallises in silky needles, melts at  $128^\circ$ , is readily soluble in alcohol and water, insoluble in ether.

*Collidinemonocarboxylic acid*,  $C_5NHMe_2.COOH + 2H_2O$ , is prepared from the ethyl salt by saponification with alcoholic potash, and evaporation to dryness of the potassium salt formed with the equivalent amount of hydrochloric acid. It crystallises in short tetragonal (?) prisms or in cube-like forms, and melts at  $110^\circ$ , or, when anhydrous, at  $155^\circ$ . It is extraordinarily soluble in water and alcohol. It has either a very faint acid reaction or none at all, and unites with acids and bases. The *potassium salt*,  $C_5NHMe_2.COOK$ , is obtained as a yellowish powder, but can be crystallised from alcohol, when it forms tufts of needles. It is very readily soluble in water and deliquesces on exposure to the air. The *calcium salt*,  $(C_5H_9NO_2)_2Ca + H_2O$ , forms a crystalline powder soluble in water. The *hydrochloride*,



crystallises in wart-like groups of needles or prisms, and is readily soluble in water or alcohol. The *platinochloride*,



crystallises in thick yellowish-red tables, melts at  $198^\circ$  with decomposition, is readily soluble in water, sparingly soluble in alcohol.

*Lutidinedicarboxylic acid*,  $C_5NHMe_2(COOH)_2 + 1\frac{1}{2}H_2O$ , is prepared by heating on the water-bath a mixture of an aqueous solution of potassium collidinecarboxylate with the amount of potassium permanganate necessary to oxidise one methyl-group, filtering off the manganic oxide separated, neutralising with nitric acid, and precipitating with lead nitrate, the lead salt being then suspended in water and decomposed with hydrogen sulphide. It crystallises in colourless, lustrous prisms, melts, when anhydrous, at  $245^\circ$ , is sparingly soluble in cold, more readily in hot water, and nearly insoluble in alcohol or ether. With silver nitrate, a solution of the ammonium salt gives a gelatinous precipitate, becoming crystalline on boiling; with lead nitrate a thick white precipitate, or from dilute solutions, after a time, rhombic tables separate, which on being boiled become transformed into short prisms. The *calcium salt*,  $C_5NHMe_2(COO)_2Ca$ , forms indistinctly crystalline crusts readily soluble in water. The *magnesium salt*,  $C_5NHMe_2(COO)_2Mg + 3H_2O$ , resembles the calcium salt. The *hydrochloride* crystallises in slender needles. The *platinochloride*,  $[C_5NHMe_2(COOH)_2]_2.H_2PtCl_6 + 6H_2O$ , crystallises in golden rhombic tables or in reddish-yellow prisms, does not melt at  $290^\circ$ , and is readily soluble in water and alcohol.

*Picolinetricarboxylic acid*,  $C_5NHMe(COOH)_3 + 2H_2O$ , is obtained

in a manner similar to the above, but with use of sufficient potassium permanganate to oxidise two of the methyl-groups in the potassium collidinecarboxylate; it is separated from any lutidinedicarboxylic acid formed at the same time by repeated crystallisation from water, in which it is the more readily soluble of the two. It crystallises in flocculent groups of slender needles, on heating becomes yellow below  $200^{\circ}$ , brown or black at  $210$ — $220^{\circ}$ , and melts with much frothing at  $238^{\circ}$ . A solution of the ammonium salt gives a gelatinous precipitate with silver nitrate; with barium chloride a voluminous precipitate; with lead and mercury salts heavy white precipitates; and with ferrous salts a yellow coloration not altered by acetic acid. The *silver salt*,  $C_5NHMe(COOAg)_3$ , is not crystalline. The *barium salt*,  $[C_5NHMe(COO)]_2Ba_3$ , forms a hard sandy powder. Picolinetricarboxylic acid does not combine with mineral acids nor yield a platinochloride. A picolinetricarboxylic acid was obtained by Besthorn and Fisher (Abstr., 1883, 600) by the oxidation of flavenol, but it is doubtful whether it is identical with the acid above described; the difference in the colour-reaction with ferrous salts and in the solubilities of the barium and calcium salts seem to indicate that it is not.

*Pyridinetetracarboxylic acid*,  $C_5NH(COOH)_4 + 2H_2O$ , is prepared from potassium collidinecarboxylate by oxidation with a quantity of potassium permanganate slightly less than that necessary for the oxidation of the three methyl-groups. Its preparation is somewhat difficult, the oxidation readily proceeding further with formation of oxalic acid and carbonic anhydride. The solution, after filtering off the manganic oxide, is neutralised with nitric acid, evaporated, and mixed with cupric sulphate, when cupric pyridinetetracarboxylate is precipitated, whilst cupric lutidinedicarboxylate and picolinetricarboxylate remain in solution. The free acid is obtained by decomposing the copper salt with hydrogen sulphide; it is still far from pure, the analytical numbers being very unsatisfactory. It crystallises in slender needles, melts with decomposition at  $188^{\circ}$ , and is sparingly soluble in alcohol and water. A solution of the ammonium salt gives with cadmium sulphate a pulverulent precipitate insoluble in hot water, with silver nitrate a gelatinous precipitate blackened by exposure to light. A solution of the acid gives with copper salts an amorphous bluish-green precipitate; with ferric chloride a yellowish flocculent precipitate; and with ferrous salts a brownish-red coloration, turning to dark cherry-red on addition of acetic acid.

A. J. G.

**Brucine.** By A. HANSEN (*Ber.*, 17, 2266—2267).—On heating brucine with hydrochloric acid, methyl chloride is given off and a substance formed which crystallises in yellowish needles melting at  $284^{\circ}$ . This when freshly precipitated dissolves readily in alkalis, and is reprecipitated by carbonic anhydride. With ferric chloride, it gives a bluish-violet, with potassium dichromate and sulphuric acid a blood-red colour, and with nitric acid a brownish-yellow precipitate. It forms a platinochloride crystallising in bronze-coloured flakes. Both the free base and its platinochloride, on analysis, yield numbers agreeing with the loss of one methyl-group from brucine. If this compound is treated with potassium hydroxide and methyl iodide, brucine

methiodide, melting at  $270^{\circ}$ , is formed identical with that obtained directly from brucine. It is thus probable that brucine contains but one methoxy-group.

L. T. T.

**Alkaloids from the Bark of Remijia Purdieana.** By O. HESSE (*Annalen*, 225, 211—262).—A preliminary notice of some of the results contained in this paper has already appeared (Abstr., 1883, 601). A description is given of the structure and properties of the bark. The alkaloids of this bark have been previously examined by Arnaud, who found about 0.2 per cent. of cinchonamine, and 0.8—1.0 per cent. of cinchonine. The author confirms the presence of these bases, but finds that several other alkaloids are present, and that the amount of cinchonine is only 0.1—0.2 per cent. The separation of the alkaloids is effected as follows: the finely divided bark is extracted with hot alcohol, the solution evaporated, and the residue after treatment with excess of caustic soda, extracted with ether. The ethereal solution is treated with excess of dilute sulphuric acid, and shaken, when the sulphates of concusconine, chairamine, conchairamine, chairamidine and conchairamidine are precipitated, (A) whilst the sulphates of cinchonine and cinchonamine with small quantities of the other bases remain in solution (B). By addition of very dilute nitric to the solution (B) cinchonamine is precipitated as nitrate and cinchonine is left in solution. The precipitate A is digested with dilute soda, and the separated alkaloids, after washing, are dried in the air, dissolved in hot alcohol, and sulphuric acid diluted with alcohol, added in the proportion of 1 part  $\text{H}_2\text{SO}_4$  to 8 parts of the alkaloids. Nearly the whole of the *concusconine* separates as sulphate, a further very small quantity separating on cooling. On adding concentrated hydrochloric acid to the cold alcoholic filtrate, *chairamine* separates as hydrochloride. The mother-liquor from this is heated, and small quantities of ammonium thiocyanate added as long as a crystalline precipitate is formed of *conchairamine* thiocyanate. After cooling and filtering, the liquid is again treated with ammonium thiocyanate, when a dark-coloured pitch-like mass separates; the filtrate from this is treated with ammonia, and the resulting precipitate shaken up with benzene. The benzene solution is shaken with dilute acetic acid, and the solution of the acetates so obtained mixed with a saturated aqueous solution of ammonium sulphate, when a precipitate of chairamidine and conchairamidine sulphates is obtained. These are separated by dissolving them in boiling water and cooling, when the whole gelatinises; on standing, crystals appear, the crystallisation being complete after some days; on now heating to  $40^{\circ}$ , the *chairamidine* sulphate dissolves, whilst *conchairamidine* sulphate is left. The process must be repeated several times on the solution to obtain a pure product.

Cinchonamine and its salts have been to some extent described by Arnaud (Abstr., 1884, 87), whose results the author in general confirms, although differing in some details. *Cinchonamine*,  $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}$ , crystallises in brilliant colourless needles, melts when anhydrous at  $184\text{--}185^{\circ}$  ( $194^{\circ}$ , Arnaud), is readily soluble in hot alcohol, ether, chloroform, carbon bisulphide, and benzene, sparingly soluble in

light petroleum and water. Its alcoholic solution has a strong bitter taste, and an alkaline reaction, and is dextrorotary:  $[\alpha]_D = +121.1^\circ$  at  $p. = 2$  and  $t. = 15^\circ$ . It dissolves in concentrated sulphuric acid with reddish-yellow colour, which slowly darkens; in nitric acid with an intense yellow. It is soluble in concentrated hydrochloric acid, but it is decomposed when heated with it in sealed tubes at  $150^\circ$ . It yields two series of salts, normal and monacid. The *hydrochloride*,  $C_{19}H_{24}N_2O \cdot HCl$ , crystallises in anhydrous colourless plates, readily soluble in alcohol, very sparingly soluble in water (according to Arnaud it contains 1 mol.  $H_2O$ ). The *platinochloride*,  $(C_{19}H_{24}N_2O)_2 \cdot H_2PtCl_6$ , is obtained as a yellow flocculent precipitate, apparently becoming crystalline after a time. The *hydrobromide*,  $C_{19}H_{24}N_2O \cdot HBr$ , crystallises in long flat needles, sparingly soluble in cold water. The *hydriodide*,  $C_{19}H_{24}N_2O \cdot HI$ , forms long colourless flat needles. The *thiocyanate*,  $C_{19}H_{24}N_2O \cdot CNSH$ , forms colourless plates or short prisms, and is very sparingly soluble in cold water. The *nitrate*,  $C_{19}H_{24}N_2O \cdot HNO_3$ , forms short colourless prisms, melts at about  $195^\circ$ , is sparingly soluble in cold water, readily in boiling water and hot alcohol. The *normal sulphate*,  $(C_{19}H_{24}N_2O)_2 \cdot H_2SO_4$ , crystallises in colourless prisms, is readily soluble in hot or cold water, very sparingly soluble in cold alcohol. Its aqueous solution is dextrorotary:  $[\alpha]_D = +36.7^\circ$  at  $p. = 2$  and  $t. = 15$ ;  $[\alpha]_D = +39.8^\circ$  at  $p. = 6$ ; and  $[\alpha]_D = +39.6^\circ$  at  $p. = 2$  and 2 mol.  $H_2SO_4$ . The *acid sulphate*,  $C_{19}H_{24}N_2O \cdot H_2SO_4$ , crystallises in anhydrous prisms and shows the rotary power  $[\alpha]_D = +34.9^\circ$  at  $p. = 2.4$  and  $t. = 15^\circ$  and  $[\alpha]_D = +37.4^\circ$  at  $p. = 6$ . The *thiosulphate*,  $C_{19}H_{24}N_2O \cdot S_2O_3H_2$ , forms anhydrous prisms sparingly soluble in water. *Acetylcinchonamine*,  $C_{19}H_{23} \cdot \overline{Ac}N_2O$ , prepared by heating cinchonamine with acetic anhydride for some hours at  $85^\circ$ , is amorphous, sinters together at  $65^\circ$ , and melts at  $89-90^\circ$ , is readily soluble in ether, alcohol, chloroform, and acetic acid. *Dinitrocinchonamine*,



is best prepared by dissolving cinchonamine in nitric acid of sp. gr. 1.06, and pouring the intensely yellow solution into an excess of very dilute ammonia. It forms yellow flocks, melts at  $118^\circ$ , is readily soluble in ether, chloroform, alcohol, and acetic acid. A solution in hydrochloric acid gives with platonic chloride a yellow flocculent precipitate of the *platinochloride*,  $[C_{19}H_{22}(NO_2)_2N_2O]_2 \cdot H_2PtCl_6 + 3H_2O$ .

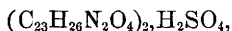
*Cinchonamine methiodide*,  $C_{19}H_{24}N_2O \cdot MeI + H_2O$ , prepared by adding methyl iodide to a solution of cinchonamine in methyl alcohol, crystallises in hard colourless prisms, readily soluble in alcohol, sparingly soluble in water. The *chloride*,  $C_{19}H_{24}N_2O \cdot MeCl$ , is amorphous. The *platinochloride*,  $(C_{19}H_{24}N_2O \cdot MeCl)_2 \cdot PtCl_4$ , is obtained as a yellow crystalline precipitate. The *hydroxide*, obtained by the action of silver oxide on an aqueous solution of the chloride, forms an amorphous mass, readily soluble in water and alcohol, sparingly soluble in chloroform and ether. It has an intensely bitter taste, and is a powerful base, eagerly absorbing carbonic anhydride from the air.

*Methylcinchonamine*,  $C_{19}H_{23}MeN_2O$ , is prepared by boiling cinchonamine methiodide, chloride, or hydroxide, with caustic soda. It forms an amorphous white powder, melts at  $139^\circ$ , is readily soluble in alcohol, ether, and chloroform, insoluble in water. The *chloride* is amorphous, the *platinochloride*,  $(C_{19}H_{23}MeN_2O)_2 \cdot H_2PtCl_6 + 4H_2O$ , is obtained as a reddish-yellow flocculent precipitate.

*Cinchonamine ethiodide*,  $C_{19}H_{24}N_2O \cdot EtI$ , forms a colourless varnish, readily soluble in alcohol, nearly insoluble in water. The *chloride* forms colourless prisms, readily soluble in alcohol and hot water. The *platinochloride*,  $(C_{19}H_{24}N_2O \cdot EtCl)_2 \cdot PtCl_4 + 2H_2O$ , forms orange-coloured crystals. The *sulphate*,  $(C_{19}H_{24}N_2OEt)_2SO_4$ , is colourless and amorphous. The *hydroxide* resembles the corresponding methyl compound.

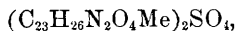
*Ethylcinchonamine*,  $(C_{19}H_{23}EtN_2O)_3 + H_2O$ , forms a white powder, melts at  $75-78^\circ$ , or when anhydrous at  $140^\circ$ , and is readily soluble in ether and alcohol. The *platinochloride*,  $(C_{19}H_{23}EtN_2O)_2 \cdot H_2PtCl_6 + 3H_2O$ , forms a reddish-yellow flocculent precipitate.

*Concusconine*,  $C_{23}H_{26}N_2O_4 + H_2O$ .—This alkaloid is obtained as the normal sulphate as already described, and is obtained in the free state by decomposition of the sulphate with dilute soda, and recrystallisation from alcohol to which a little ammonia has been added. It forms colourless or pale-yellow compact prisms. It is readily soluble in ether, chloroform, and benzene, sparingly soluble in boiling alcohol, insoluble in water. It is optically dextrorotary, giving for  $C_{23}H_{26}N_2O_4 + H_2O$ ,  $p. = 2, t. = 15^\circ$ ; in 97 vol. per cent. alcohol  $[\alpha]_D = 40.8^\circ$ . The hydrate melts at  $144^\circ$ , becomes anhydrous, and then melts again at  $206-208^\circ$ ; at  $140-150^\circ$  it becomes dark-brown coloured, being in small part converted into amorphous concusconine. (This amorphous concusconine is readily separated by conversion of the fused mass into the normal sulphates, treatment with alcohol in which the sulphate of the amorphous base is readily soluble, and precipitation with ammonia, when it separates in dark-brown, amorphous, readily fusible flocks.) Concusconine dissolves readily in acetic anhydride apparently without formation of an acetyl-derivative; from this it seems that no hydroxyl-groups are present. Nitric acid converts it into a dark-green mass; addition of nitric acid to its solution in acetic or hydrochloric acids gives the dark-green coloration characteristic of this group of alkaloids. Concentrated sulphuric acid dissolves concusconine with bluish-green colour, becoming olive-green on heating. With chromic acid and sulphuric acid, it gives a coloration at first dark reddish-brown, then intensely dark-green. Although concusconine is tasteless, its solutions in acids have a bitter taste. The salts are as a rule gelatinous. The *platinochloride*,  $(C_{23}H_{26}N_2O_4)_2 \cdot H_2PtCl_6 + 5H_2O$ , is obtained as a voluminous yellow flocculent precipitate. The *normal sulphate*,



forms small white prisms nearly insoluble in water and alcohol in the cold, sparingly soluble on heating. The *acid sulphate* is a gelatinous mass readily soluble in hot water. By mixing an alcoholic solution with methyl iodide, and allowing it to stand 24 hours, there is

obtained a mixture of two *iodides* in about equal quantities; they can be separated by the difference of their solubilities in hot alcohol. The less soluble  $\alpha$ -compound forms microscopic hexagonal prisms of the formula  $C_{23}H_{26}N_2O_4, MeI$ , very sparingly soluble in hot alcohol, moderately soluble in boiling water. By treatment with silver chloride, it is converted into the *chloride*,  $C_{23}H_{26}N_2O_4, MeCl$ , crystallising in microscopic needles, readily soluble in water and alcohol. The *platinochloride*,  $(C_{23}H_{26}N_2O_4, Cl)_2, PtCl_4 + 4H_2O$ , forms a yellowish-red flocculent precipitate, and is insoluble in water. The *aurochloride* forms a dirty yellow flocculent precipitate, from which gold soon separates. The *sulphate*,  $(C_{23}H_{26}N_2O_4)_2SO_4$ , formed by the action of silver sulphate on the iodide, is amorphous and very readily soluble in water and alcohol. Its rotary power in aqueous solution at  $p. = 3.764$  and  $t. = 15^\circ$  is  $[\alpha]_D = +73^\circ$ . The *hydroxide*,  $C_{23}H_{26}N_2O_4, Me.OH + 5H_2O$ , obtained by the action of baryta-water on the sulphate, crystallises in colourless cubes, melts at  $202^\circ$ , is readily soluble in alcohol and boiling water, insoluble in ether. The *iodide* of the  $\beta$ -compound,  $C_{23}H_{26}N_2O_4, MeI$ , is gelatinous and dries in air to a horny mass; is somewhat soluble in boiling water, readily soluble in alcohol. The *chloride* is amorphous. The *platinochloride*,  $(C_{23}H_{26}N_2O_4, MeCl)_2, PtCl_4 + 5H_2O$ , is a reddish-yellow flocculent precipitate. The *sulphate*,

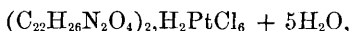


is a brown amorphous mass, and has no action on polarised light. The *hydroxide*,  $C_{23}H_{26}N_2O_4, Me.OH + 2\frac{1}{2}H_2O$ , forms a brown amorphous mass, readily soluble in cold water and alcohol.

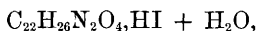
*Chairamine*,  $C_{22}H_{26}N_2O_4 + H_2O$ , crystallises in white needles or thick colourless prisms, and melts at  $140^\circ$ , or when anhydrous, at  $233^\circ$ . It is readily soluble in ether and chloroform, 1 part of the base dissolves in 540 parts of 97 per cent. alcohol. The alcoholic solution is strongly dextrorotary ( $[\alpha]_D = \text{about } 100^\circ$ ). Dissolved in sulphuric acid containing molybdic acid, the solution at first colourless becomes after a time an intense dark-green. The *hydrochloride*,  $C_{22}H_{26}N_2O_4, HCl + H_2O$ , crystallises in colourless needles, sparingly soluble in boiling water and alcohol, insoluble in dilute hydrochloric acid. The *platinochloride*,  $(C_{22}H_{26}N_2O_4)_2, H_2PtCl_6 + 2H_2O$ , forms yellow needles insoluble in water and alcohol. The *normal sulphate*,  $(C_{22}H_{26}N_2O_4)_2, H_2SO_4 + 8H_2O$ , forms concentric groups of colourless needles, sparingly soluble in cold water or alcohol. The *thiocyanate* forms white needles insoluble in water.

*Conchairamine*, crystallises with both water and alcohol of crystallisation in thick colourless prisms of the formula  $C_{22}H_{26}N_2O_4 + H_2O + C_2H_6O$ , the compound showing three melting points, namely,  $82-86^\circ$  for the whole compound,  $108-110^\circ$  after expulsion of the alcohol, and about  $120^\circ$  for the anhydrous compound, the mass resolidifying between each temperature. A small portion is converted by the heating into amorphous conchairamine. Conchairamine is readily soluble in hot alcohol, in ether, and chloroform, sparingly soluble in cold alcohol. Its solution in 97 per cent. alcohol has a rotary power  $[\alpha]_D = +68.4^\circ$  at  $p. = 2$  and  $t. = 15^\circ$ . The alcoholate dissolves in sulphuric acid containing molybdic acid, giving a brown

coloration that soon becomes intensely dark-green. With potassium chromate and sulphuric acid, it gives a coloration at first reddish-brown, then dark-green, and reddish-yellow if boiled with excess. The *hydrochloride*,  $C_{22}H_{26}N_2O_4 \cdot HCl + 2H_2O$ , crystallises in colourless plates, readily soluble in hot water and alcohol, sparingly soluble in cold water, nearly insoluble in ether. The *platinochloride*,



forms a dark-yellow flocculent precipitate. The *hydroiodide*,

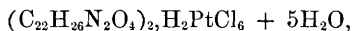


crystallises in colourless needles, sparingly soluble in cold water. The *thiocyanate* crystallises in colourless needles, very sparingly soluble in hot water. The *sulphate*,  $(C_{22}H_{26}N_2O_4)_2 \cdot H_2SO_4 + 9H_2O$ , crystallises in long lustrous prisms, soluble in boiling water. The *nitrate* forms satiny plates or needles very sparingly soluble in water.

*Conchairamine methiodide*,  $C_{22}H_{26}N_2O_4 \cdot MeI$ , is obtained either in red crystals containing 1 mol.  $H_2O$ , or in colourless crystals with  $3H_2O$ . The *chloride*,  $C_{22}H_{26}N_2O_4 \cdot MeCl + 2H_2O$ , crystallises in large colourless rhombohedrons, readily soluble in water and alcohol. The *platinochloride* has the complex formula  $(C_{22}H_{26}N_2O_4 \cdot MeCl)_2 \cdot PtCl_4 + (C_{22}H_{26}N_2O_4 \cdot MeHCl_2) \cdot PtCl_4 + 14H_2O$ ; it crystallises in orange-coloured needles, and is insoluble in cold water. The *nitrate* forms colourless satiny plates. The *hydroxide* formed by the action of moist silver oxide on the chloride, forms an amorphous brown mass of bitter taste, readily soluble in water, insoluble in ether.

*Chairamidine*,  $C_{22}H_{26}N_2O_4 + H_2O$ , forms an amorphous white powder, melts at  $126-128^\circ$ , and is readily soluble in ether, alcohol, benzene, and chloroform, insoluble in water. Its alcoholic solution shows the rotary power  $[\alpha]_D = +7.3^\circ$  at  $p. = 3$  and  $t. = 15^\circ$ . It dissolves in concentrated sulphuric acid with yellowish colour, which later turns dark-green. The *platinochloride*,  $(C_{22}H_{26}N_2O_4)_2 \cdot H_2PtCl_6 + 5H_2O$ , forms yellow amorphous flocks insoluble in water. The *normal sulphate* and *hydrochloride* are gelatinous, the *acetate* forms a slimy mass.

*Conchairamidine*,  $C_{22}H_{26}N_2O_4 + H_2O$ , crystallises in white needles, melts at  $114-115^\circ$ , and is very readily soluble in ether, chloroform, alcohol, benzene, and acetone. Its solution in alcohol (97 per cent.) is levorotary,  $[\alpha]_D = -60^\circ$  at  $p. = 3$  (anhydrous) and  $t. = 15^\circ$ . It dissolves in concentrated sulphuric acid with an intense dark-green colour. With chromic and sulphuric acids, it gives a solution at first brown, then dark-green. The *hydrochloride*,  $C_{22}H_{26}N_2O_4 \cdot HCl + 3H_2O$ , crystallises in long colourless needles. The *platinochloride*,



forms a yellow flocculent precipitate. The *normal sulphate*,



crystallises in long colourless needles, sparingly soluble in cold water. The *thiocyanate* is amorphous, readily soluble in alcohol, and sparingly soluble in cold water.

The substance described under the name of concusconidine in the author's earlier communication (*loc. cit.*) has been found to be a mixture of alkaloids.

A. J. G.

**Preparation of Albumin.** By W. MIHAILOFF (*Bull. Soc. Chim.*, **41**, 547—548).—The author describes a new method for obtaining pure albumin. White of egg, filtered through muslin, is treated with three times the quantity of a saturated solution of ammonium sulphate, and to this as much more solid ammonium sulphate is added as will dissolve. The albuminoid substances (globulins, globulins, and albumin) are thus precipitated. The precipitate is washed with a saturated solution of ammonium sulphate, and, having been rendered slightly alkaline with ammonia, is dialysed. The water which replaces the excess of sulphate and the alkalis of the precipitated albuminoids, leaves the whole of the globulins and globulins in the precipitate, and the pure albumin is obtained in solution. This solution may be boiled without coagulation taking place, is almost neutral in its reaction (slightly acid), and gives no precipitate with barium salts. By means of ammonium sulphate, all albuminoids and their derivatives may be precipitated.

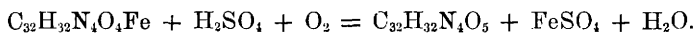
A. B.

**Colouring Matter of the Blood.** By M. NENCKI and N. SIEBER (*Ber.*, **17**, 2267—2276).—The authors find that the use of amyl alcohol as a solvent forms a very good method for obtaining hæmin from blood. Freshly defibrinated blood is mixed with a solution of salt and allowed to stand for 24—40 hours in shallow dishes. It is then mixed with double its volume of 99 per cent. alcohol, and stirred well until thoroughly coagulated. The coagulated mass is allowed to stand another 24 hours, and then filtered off and spread on blotting-paper. It should not be allowed to get too dry, and is usually dry enough after exposure to the air for about 24 hours, when it should still lose about 60—65 per cent. of water if dried at 110°. This partly dried mass is then powdered in a mortar, 400 grams are introduced into a flask with 1600 grams of amyl alcohol, and the whole heated to boiling; 25 c.c. of pure hydrochloric acid of sp. gr. 1.12 are then added, and the whole boiled for 10 minutes and filtered. As it cools, the amyl alcohol deposits the hæmin as hydrochloride in thin glittering rhombic plates. These should be washed with alcohol and ether, and dried at 105°. 1.5—3 grams of pure crystals are obtained from 3 litres of blood. In this way, hæmin was prepared and analysed from human blood, the blood of the ox, horse, and dog. In each case some of the crystals were converted into hæmatin by solution in caustic soda and precipitation with hydrochloric acid. All these specimens of hæmatin from different sources were also analysed. In all cases when the hæmin crystals were dissolved in alkali, amyl alcohol was liberated, and it was found that when prepared as above hæmin always contains amyl alcohol of crystallisation, which it loses neither by digestion with alcohol nor by drying at 110°. The crystals do not change in composition even when digested with dilute hydrochloric acid. The analyses of the samples from various sources gave numbers agreeing very closely, and leading to the formulæ



( $C_{32}H_{30}N_4FeO_3, HCl$ )<sub>2</sub>,  $C_5H_{12}O$  for hæmin hydrochloride crystals, and  $C_{32}H_{32}N_4FeO_4$  for hæmatin; so that the latter is produced from hæmin by the addition of the constituents of water. The properties of the hæmatin obtained as above agree with those ascribed to this compound by Hoppe-Seyler. From the ease with which hæmin forms double compounds with indifferent bodies such as amyl alcohol, the authors think it probable that its composition varies according to the method of preparation; and that the various hæmoglobins are possibly such double compounds of hæmin with albumins.

Concentrated sulphuric acid deprives hæmatin of its iron, and Hoppe-Seyler, who named the resulting compound hæmatoporphyrin, ascribed to it the formula  $C_{88}H_{74}N_4O_{12}$ —a more highly hydrogenised formula than that which he ascribed to hæmatin. The authors find that the real formula of hæmatoporphyrin is  $C_{32}H_{32}N_4O_5$ , and that it is formed according to the equation—



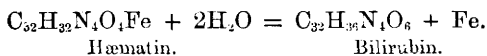
Hæmatoporphyrin is obtained much more easily by treating hæmin crystals with concentrated sulphuric acid. Hydrochloric acid is evolved, the crystals dissolve, and the solution deposits hæmatoporphyrin. Hæmatolin, which is the product of the action of strong sulphuric acid on hæmatin out of contact with the air, is neither soluble in acids nor in alkalis, and has not been further investigated.

When subjected to the action of reducing agents, hæmin and hæmatin yield various reduction-products according to the nature of the reducing agent, the temperature employed, &c. With tin and hydrochloric acid, the chief product is *hexahydrohæmatoporphyrin*,  $C_{32}H_{38}N_4O_5$ , which is formed from hæmin crystals, according to the equation



It is a brownish-red pigment, easily soluble in alcohol, sparingly in dilute hydrochloric acid, insoluble in water and alkalis. When boiled with alcoholic potash, it is converted into a product easily soluble in aqueous alkalis, and very closely resembling urobilin in properties. The authors are now investigating this compound, which also appears to be formed in small quantities during the reduction of hæmin with tin and hydrochloric acid. By long-continued boiling with tin and hydrochloric acid, a solution of hæmin becomes quite colourless, volatile substances with odours resembling pyridine being formed. Attempts to obtain oxidation-products of hæmatin proved fruitless, nothing but oxalic and carbonic acids being obtained. Leyer and Köller state (*Ber.*, 7, 1064) that hæmatin is split up by dilute sulphuric acid into lucine and tyrosine. When fused with caustic potash—towards which it is very stable—hæmatin gives off ammonia and pyrroline, but no lucine is formed. Leyer and Köller were probably dealing with impure hæmatin.

The colouring matter of the blood is undoubtedly allied to the colouring matter of the bile, and the conversion may be expressed by the equation

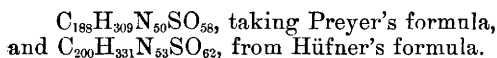


Whether hæmatin is converted in the liver into bilirubin or bilirubin into hæmatin and hæmin is at present very doubtful, but the authors are much inclined, from analogy with the formation of glycogen from dextrose, &c., to think the latter more likely.

L. T. T.

**Studies on Blood.** By H. STRUVE (*J. pr. Chem.* [2], **29**, 305—350).—The author contests the hitherto accepted view of the composition of blood-crystals, which according to Preyer are oxyhæmoglobin, of the formula  $C_{600}H_{960}N_{151}FeS_3O_{179}$ . The author finds that these crystals are rendered insoluble by treatment with alcohol, without changing their form, and that they can then be further decolorised by treatment with alcoholic ammonia, glacial acetic acid, strong sulphuric acid, or chlorine water, and therefore regards them as crystals of a colourless albuminous substance accompanied by a minute quantity of one or more blood colouring matters. By extracting with ether, water, and alcohol respectively, the author has obtained from the blood-corpuscles three distinct groups of compounds. The portion soluble in ether is, at ordinary temperatures, a brown mass, which is generally soapy but sometimes crystalline. When heated, it melts and burns, emitting an odour of fat and acraldehyde; the ash contains traces of phosphoric acid but no iron. Its solution gives an absorption-band in the red, and it contains cholesterin, lecithin, cerebrin, and glycerides. The aqueous extract, on the other hand, leaves on evaporation an amorphous mass of dark colour, readily soluble in alcohol and water, but only slightly so in ether. Its solution gives a strong absorption-band corresponding with Preyer's oxyhæmatin alkali; it gives no precipitate with lead acetate or mercuric chloride in the cold, but the colouring matter is completely precipitated on boiling. Acids produce a precipitate even in the cold; this is readily soluble in alkalis and alkaline carbonates without evolution of ammonia. It gives no hæmin-crystals; the ash contains ferric oxide, phosphoric acid, and silica. Elementary analyses of the colouring matter point distinctly to its being a mixture of several substances. The author regards the colouring matter as a feeble acid, which is probably combined in the blood with soda or some organic base, and proposes to name it *hæmatic acid*. The third group of substances is obtained from the corpuscles by extraction with alcoholic ammonia, and is represented by a single crystalline colouring matter, which is quite insoluble in water, alcohol, ether, and dilute acids, sparingly soluble in dilute ammonia; the ash consists almost wholly of ferric oxide. The alkaline solutions of the colouring matter exhibit the spectrum of Preyer's oxyhæmatin-alkali; on adding an acid, the colouring matter is precipitated quantitatively in an amorphous state; this colouring matter yields hæmatin-crystals. The elementary analysis corresponds with the empirical formula  $C_{70}H_{64}N_8Fe_2O_{10}$ , which agrees very closely with Hoppe-Seyler's formula for hæmatin,  $C_{68}H_{70}N_8Fe_2O_{10}$ . The author is of opinion that the hæmatin analysed by Hoppe-Seyler was impure, and that the carbon and hydrogen were consequently low. Owing to its behaviour with alkalis, the author regards this crystalline colouring matter as a feeble acid, and proposes for it the name of

*hæmic acid.* The blood-crystals are thus to be considered as crystals of a blood-albumin (globulin-crystals) free from iron, which are coloured by a definite quantity of hæmatic and hæmic acids. The quantitative determination of these two acids is at present impossible, but supposing the colouring matter to be entirely hæmic acid, and if the proportion of iron in the blood-crystals be 42 per cent., and in hæmic acid 8.71 per cent., then the blood-crystals are composed of globulin-crystals 95.18 per cent., hæmic acid 4.82 per cent. Moreover, since the above empirical formulæ, both of the blood-crystals and of hæmic acid, are calculated from the proportion of iron they contain, the difference between the two must be the empirical formula of the globulin-crystals—



It is at present impossible to decide between the above formulæ, but it is especially interesting that the percentage composition indicated by either of them corresponds in a remarkable manner with that given by Gorup-Besanez for the albuminoids in general.

According to the author's theory, all the spectroscopic phenomena exhibited by solutions of blood are due exclusively to the colouring-matters, hæmatic and hæmic acids; he has not, however, succeeded in artificially producing by means of mixtures of these two bodies, the bands  $\alpha$  and  $\beta$ , which are characteristic of oxyhæmoglobulin, and which are exhibited by all fresh solutions of blood. All the other spectroscopic phenomena of blood solutions, *e.g.*, the spectra of hæmoglobin, metahæmoglobin, and hæmochromogen, are to be regarded as spectra of certain definite products of oxidation, reduction, or decomposition of hæmatic and hæmic acids.

P. F. F.

### Physiological Chemistry.

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**Digestibility of Potatoes and Carrots with Hay and Oats by the Horse.** By E. WOLFF and others (*Bied. Centr.*, **184**, 615—617).  
 —The following are digestive coefficients of potatoes and carrots consumed by two horses, the second having received only the carrots in conjunction with hay and oats, for the first died from colic during the “potato” period :—

	Dry matter.	Organic matter.	Albumin.	Fibrin.	Non-nitrogen. matter.
Potatoes....	90·46	93·28	88·01	9·14	99·36
Carrots ....	84·86	87·23	99·31	—	93·81

Compared with the digestive coefficients of sheep and pigs for potatoes—

	Organic matter.	Albumin.	Non-nitrogen. matter.
Sheep.....	87·5	65·1	92·8
Pig .....	93·3	72·5	98·0

the comparison is much in favour of the horse.

Referring again to the experiments, we find that carrots greatly assist the digestion of the fibre of hay, and that oats rather reduce the digestion of hay fibre, viz., 44·65—38·42, but that the percentage again rises when the carrots are consumed with the oats and hay.

E. W. P.

**Elimination of Phosphoric Acid in the Urine in Insanity and Epilepsy.** By A. LAILLER (*Compt. rend.*, 99, 572—573).—The author's results, obtained from many hundred analyses made whilst resident officer in a large asylum, agree with those of Mairat. In acute delirium, phosphoric acid and urea are eliminated in notable excess; in excitable mania, the phosphoric acid is in slight excess, whilst the amount of urea is normal; and in simple insanity the urine has the normal composition. In acute or excitable lypemania, the amount of urea eliminated is abnormally high, whilst that of phosphoric acid is abnormally low. In simple lypemania, the composition of the urine is normal. In general paralysis, the elimination of both phosphoric acid and urea is related to the general morbid conditions of the patient. At or immediately after epileptic seizures, the urine contains a high proportion of phosphoric acid and a low proportion of urea. If the seizures succeed one another rapidly, the proportion of both phosphoric acid and urea is increased; but in the interval between seizures the urine has the normal composition.

C. H. B.

**Influence of Exhausted Beetroot Pulp on Cow's Milk.** By A. ANDOUARD and V. DÉZAUNAY (*Compt. rend.*, 99, 443—445).—When beetroot pulp, exhausted by diffusion and preserved in silos, is employed as part of the food of cows, the yield of milk is considerably increased, and the animals themselves gain in weight, the increase in both cases depending on the particular animal and the nature of the other constituents of its food. The proportion of butter is likewise augmented, and apparently its quality is not affected. On the other hand, if the pulp is given in large quantity without admixture of a sufficient proportion of green food, the milk has a disagreeable taste, and is much more liable to spontaneous coagulation. These defects are probably shared by other easily fermentable foods, and it follows that such substances are to be avoided if the milk is required for drinking or cooking purposes, but are advantageous when the production of butter or the fattening of the beast is the main object.

C. H. B.

**Various Cattle Diseases.** By EGGELING and PASTEUR (*Bied. Centr.*, 1884, 540—544).—Eggeling describes two diseases to which swine are liable; both are of the nature of erysipelas, one contagious, the other not. He throws no light on their origin, prevention, or cure. He also draws attention to a disease to which horned cattle

are subject on farms attached to distilleries of potato-spirit, due to over-eating the refuse and its fermentation.

Pasteur gives further information respecting his experiments on hydrophobia. When the virus from a mad dog is communicated to an ape, from this to another, and so on, the poison becomes so weakened that when again injected hypodermically into another dog it is incapable of producing madness, and even when introduced into the brain by trepanning, an operation which hitherto has always been followed by madness, it failed and, on the other hand, rendered the animal invulnerable against the disease. When, however, the virus is passed into the bodies of rabbits or guinea-pigs, its intensity is increased by each inoculation, and after a few such, when again communicated to the dog produces madness of a very much more dreadful type, and death invariably follows. Although the virus is weakened when passed into the bodies of monkeys, it can be made to resume its virulence by inoculating rabbits or guinea-pigs from the monkey, and so on until it is again passed to a dog, producing madness and death.

Pasteur suggests a means of utilising the action of the virus on rabbits—from a dead rabbit he inoculates a live one, from that a second, and so on; but from each of these animals he inoculates a dog (the same dog), the poison increases in virulence at each operation, but the dog has passed through the previous stage and is not harmed, so that when the intensity of the virus is at its maximum the dog bears it without hurt, although it would madden and kill another not so prepared. J. F.

**Physiological Effect of Lead on Ruminants.** By ELLENBERGER and HOFMEISTER (*Bied. Centr.*, 1884, 536—540).—The chronic effects of repeated doses of lead on domestic animals has not been much studied; lead salts, as is well known, have a strong affinity for albumin, and when taken even in very small quantities the accumulation of lead albuminate in the system produces serious effects.

Sheep were the animals experimented on, and the salt of lead employed was the acetate, in doses of 0.5 to 3 grams per day, gradually increasing from the smaller quantity. The symptoms of lead sickness in the sheep are not remarkable, loss of appetite, apathy, disturbed rumination, muscular weakness, dry dull wool, diminution of urine and of urea, disappearance of hippuric acid, presence of albumin in the urine, and protruding bowel.

To determine the presence of lead in the organs, the author incinerates, extracts with nitric acid, and precipitates with sulphuretted hydrogen. The quantity contained by different organs varies considerably, as much was found in the kidneys as in the liver, contrary to expectation—one would expect most in the liver, the metal coming earlier into contact with it by means of the portal vein. After the kidneys and liver, most metal is found in the salivary glands and pancreas, then follow the bones and nervous system; the blood and muscular system were poor in lead, but the spleen held a comparatively large quantity. The author thinks the poison attacks the nervous system first, and then the muscular. Excretion takes place

by the kidneys, liver, pancreas, and saliva, according to the preparation of lead employed ; it is perceptible in the urine in about 40 hours.

J. F.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Nitrogen necessary for Cultivated Plants.** By THAER (*Bied. Centr.*, 1884, 546—549).—The author in 1879 reported to a congress of naturalists at Freiburg, as the result of eleven years' experiments, that the nitrogen contained in the crops on which he experimented, grown on sandy loam, was derived from the soil, to half its amount. He has continued his experiments since then on potatoes, rye, barley, and peas, and now arrives at the conclusion that there is an unmistakable relation between the quantity of nitrogen supplied by the soil and that put into it by man.

If man supplies nitrogen freely in the manure, nature responds freely in the crop; if man is sparing, so is nature; and he formulates the rule that in a year of fairly productive weather, if the farmer supplies in the form of manure one-half the nitrogen which he ought to receive from the crop, that nature will supply the remainder. He excepts specially adverse seasons when, for example, exceptional dryness prevents decomposition of nitrogenous substances; in such cases, sulphate of ammonia and Chili saltpetre, if used, are a complete loss, as they are never available after the first year. J. F.

**Formation of Sugar in Beets.** By A. GIRARD (*Bied. Centr.*, 1884, 545—546, and *Compt. rend.*, 99, 808).—The author being of opinion that light takes a very great part in the production of cane-sugar in the beet, undertook a series of experiments, extending over several months. He had leaves gathered daily about four o'clock in the afternoon and three in the morning, and analysed them; he found that the leaves gathered after the enjoyment of the whole day's light invariably contained considerably more cane-sugar than those plucked after passing through the night, the amount in the former being in all cases more than double that of the latter; the glucose and reducing sugars did not vary in anything like the same proportion. He considers the leaves to be the place where the sugar is formed, from whence it passes to the roots, and that a double process of osmose is continually being carried on within the cells of the plant, one carrying the mineral matters derived from the plant to the leaves, the other bringing the completed saccharose to the roots. Tollens agrees with him in this view, which he says has long been accepted as true.

In a paper recently published in the *Comptes rendus*, the author gives additional experiments confirming these results. J. F.

**Salicylic Acid in the Cultivated Pansy.** By A. B. GRIFFITHS and E. C. CONRAD (*Chem. News*, 50, 102).—Various parts of the



garden pansy were found to contain the following percentage of salicylic acid :—

	I.	II.
Leaves .....	0·1329	0·1330
Stems.....	0·0852	0·0856
Roots.....	0·0531	0·0529

D. A. L.

**Experiments with Manures containing Thiocyanates.** By G. KLEIN (*Bied. Centr.*, 1884, 519—520).—Three plots were sown with barley and oats, one remained unmanured, the second was manured with ammoniacal superphosphate, the third was manured with the same, receiving in addition 0·8 per cent. of ammonium thiocyanate. In the last plot, the plants were developed slowly, and the points of the leaves became brown; this lasted two weeks, when rain came on, and the plants recovered their normal strength and appearance, and they flourished as well as those in the other plots; evidently the rain had caused decomposition of the thiocyanate. With water culture, the nutritive liquid used contained 0·01 gram of ammonium thiocyanate to the litre; old plants with six to eight leaves bore this without injury, but when the quantity was doubled they sickened at once, and 0·1 gram per litre proved fatal almost immediately. In view of the decidedly poisonous effects of the thiocyanate, the author cautions farmers against using manures containing it. J. F.

**Poisonous Effects of Ammonium Thiocyanate on Vegetation.**

By J. KÖNIG (*Bied. Centr.*, 1884, 520—522).—Four flower-pots were filled with loamy soil, each was manured with 8 grams ammoniacal superphosphate. No. 1 was left so, No. 2 received 0·05 gram, No. 3 0·10 gram, and No. 4 0·25 gram of ammonium thiocyanate; they were put aside for five weeks, at the end of which No. 1 had a plentiful crop of weeds; No. 2 only a few, and the other two none. The weeds were removed, and the pots sown with barley and oats. The growth was good in all of the pots, and the pots containing thiocyanate surpassed the others, owing probably to the excess of ammonia and decomposition of the thiocyanate. Similar experiments were made, sowing manure and seeds together; the results were similar, and were confirmed by others in which the plants were watered with solutions containing varying quantities of thiocyanate. The author cautions buyers of manures against the use of certain superphosphates now being actively pushed, and if they are used advises them to be sown some days before the seed; if possible rainy weather should intervene. J. F.

**Influence of Acid Smoke on Vegetation.** By J. v. SCHROEDER and another (*Bied. Centr.*, 1884, 555—556).—The damage done to growing plants by smoke containing acid gases shows itself first by the leaves becoming yellow or yellowish-brown and spotted—in leaves of the pine family the points become yellow. Such parts on analysis yield larger proportions of sulphuric or hydrochloric acid, as the case may be, than the healthy leaves. Schroeder says that  $\frac{1}{1000}$  of sul-

phurous anhydride in the air will quickly injure plants, but plants are not so sensitive to hydrochloric acid. The most sensitive to sulphurous gas are coniferous trees, the least so agricultural plants and vegetables. Fruit trees are very liable to damage, plums and cherries more so than apples or pears.

The author made a large number of analyses of affected trees in the neighbourhood of four different factories, in two of which zinc blende was roasted, a bronze foundry, and a general chemical works for producing sulphuric and hydrochloric acids, chloride of lime, &c.; he found that all the plants whose leaves showed they had been attacked, contained throughout their substance more of the acids than healthy plants. To meet the suggestion that the supply came from the soil, he made several examinations of it also, the results of which confirm his views. On examination of the ash for carbonic acid, less was found than in healthy plants; the author thinks it proved that the acid gases penetrating from the exterior to the interior of the plant neutralise the inorganic and organic bases necessary to growth, and substitute those of a hurtful character.

J. F.

**Use of Copper Sulphate to Destroy Mildew.** By A. PERREY (*Compt. rend.*, 99, 543—545).—When vine poles are steeped in a strong solution of copper sulphate, and vines of from four to six years old are carefully trained round them, the vines are protected from mildew (*Peronospora viticola*), but the efficacy of the copper sulphate does not extend beyond a cylindrical space 0·2—0·25 metre in diameter, having the vine pole for its axis.

C. H. B.

**Carbon Bisulphide in Aqueous Solution as a Remedy for Phylloxera.** By E. PELIGOT (*Compt. rend.*, 99, 587—591).—The author confirms Ckiandi-Bey's observations respecting the antiseptic properties of carbon bisulphide. He finds that when carbon bisulphide is briskly agitated with water at the ordinary temperature, 100 c.c. of water dissolve 0·35 c.c., or 0·452 gram of carbon bisulphide. The solution has no action on lead paper, but when boiled *rapidly for some time* it gives off its carbon bisulphide, and the condensed water contains small quantities of hydrogen sulphide. The author recommends the application of an aqueous solution of carbon bisulphide to vines instead of the liquid itself.

C. H. B.

**Protective Influence of Growing Plants on the Undergrowth.** By E. WOLLNY (*Bied. Centr.*, 1884, 550—551).—The distribution of water in the soil, and the temperature, depend very much on whether it is in a state of cultivation or not; in fallow ground, the higher strata are the drier, and the lower the more moist. When covered by vegetation, the contrary is the case, as the roots of the plants withdraw moisture from the subsoil, and the leaves, fruit, &c., of the growing plants protect the upper layer from the drying influences of sun and wind. Small seeds which are near the surface fare badly in fallow ground, but when sown where they are protected by vegetation they grow well. As soon as their roots reach the lower layers occupied by the

roots of the covering plants, these must be removed, as well on account of the exhaustion of moisture as of excess of shade.

J. F.

**Four-course System at Woburn.** By A. VOELCKER (*Bied. Centr.*, 1882, 623—626; *Jour. Agri. Soc.*, 19, 348—356).—This report refers to the season 1883, and is an account of experiments conducted in the same manner as has been previously reported on and referred to in this Journal. The highest yield of purple top swedes was obtained from the plot (plot 3) manured with farmyard manure of known composition mixed with Chili saltpetre, bone-ash, superphosphate, and sulphates of magnesium and potassium, the lowest yield (plot 1) from the plot which had received farmyard manure (cotton cake added to the food); on the second plot, grew Dutch white clover, and it was fed off by sheep which on plot 1 received also cotton cake, and on plot 2 maize-meal; the sheep on plot 1 increased in weight the most rapidly of all the flock, and this greater increase is due to the cake. The clover on 3 was of least value, the action of the saltpetre showing itself by diminishing the value of the succeeding season. The wheat was lowest on plot 3, but the straw was highest; but the barley was highest of plot 2, which had received only farmyard manure made with maize-meal. E. W. P.

**Growth of Breadstuffs in Various Latitudes.** (*Bied. Centr.*, 1884, 626—628).—In Europe, barley (and potatoes) can be grown as far north as 70°, but east and westwards the limit falls southwards. In the Faroe Islands (61—63°) but little grain is grown, whilst in Greenland and Iceland none at all. In East America the limit is 50°, which rises to 57—58° on the western coast, whilst on the east coast of Asia it again sinks to 50°, gradually rising to 60° (Obi river), 67° Archangel, and finally in Sweden to 70°. In the southern hemispheres, the regions of limited growth are not ascertained. The latitude does not wholly determine the limit, height above the sea must also be taken note of. In Sweden, cereals will not grow at a height above a few metres, whilst in Switzerland they flourish at a height of 625—1250 metres; wheat requires a higher temperature than rye or barley, oats require least warmth. There are many districts in the Alps where by reason of the cold no winter corn can be sown, yet the summers are hot enough for maize to grow well. In the Himalayas, maize is grown at 938 metres, wheat at 3125 metres, barley, oats, and rye at 3750 metres, and in Thibet wheat ripens at 5625 metres. The change in the temperature is remarkable. Proceeding eastwards, wheat again becomes more nitrogenous, which fact is accounted for by the harder winters, the hotter summers, and the smaller amount of rain than is experienced in Europe. The following figures represent the percentages of nitrogen in several samples of wheat:—

Scotch, 2·01; North of France, 2·08; Lille, 2·18; Chemnitz, 2·42; Bavarian, 2·20; Eldena, 2·18; Moravian, 2·36; Polish, 2·68; Odessa, 3·12; Tayanzog, 2·54; Rjāsan, 2·47; Samara, 3·47; European Russia, 3·58; Wilna, 1·95; Central Provinces, 3·57; South-eastern Provinces, 3·72; Siberia, 2·65; Tobolsk, 2·74. The nitrogen in rye and barley

also varies: Scotch rye, 0.90; German, 2.12; Scotch barley, 1.42; Bavarian, 1.72. E. W. P.

**Cultivation of two Varieties of Sorghum, and Preparation of Sugar therefrom.** By V. PFUEL and another (*Bied. Centr.*, 1884, 628—630).—*Holcus sorghum* and *H. saccharatum* were sown thin and on the flat; the method of cultivation is the same as for maize, and after autumn cutting it throws up a good feed for sheep. As regards the value of this crop as a source of sugar, it has been found that at the period when the seed ripens there is 15 per cent. of saccharose present; before that time the quantity is only 1—3 per cent. That the yield of sugar may be as high as possible, the rows should be 4 feet apart, the seeds (six together) one inch deep, and each plant left at 4 to 6 inches apart from its neighbour. The rows should run north and south, and the land be kept well hoed until the plants are 3 to 4 feet high. E. W. P.

**Cultivation of Sorghum in France.** By N. MINANGOIN (*Bied. Centr.*, 1884, 634).—The cultivation of sorghum is less costly than that of beet, and the yield of molasses is less. By the use of Champonnois' apparatus, good brandy can be prepared, and the residue makes good fodder, but the brandy must be thoroughly rectified, which can be accomplished without difficulty. E. W. P.

**Drying of Diffusion Cuttings.** By M. MÄRCKER and others (*Bied. Centr.*, 1884, 630—632).—Hellriegel states that it is advisable to dry these cuttings thoroughly at a high temperature, after which they absorb but a relatively small amount of moisture, and keep better. Märcker thinks that the digestibleness is impaired by the high heating; he also recommends  $\frac{1}{2}$  per cent. of lime to be added, and then pressure applied before drying; this prevents swelling, and renders the pressing more easy of accomplishment. Cunze and Stammer consider that this addition renders the fodder unpalatable; moreover, this  $\frac{1}{2}$  per cent. is equivalent to 10 per cent. of calcium carbonate when the sections are dry. Märcker, on the other hand, says cattle eat the fodder with vigour, and that the lime only amounts to 4.4 per cent., as part is removed by pressing—of the remainder 1.1 per cent. only is as carbonate, the rest being present as organic salt; also clover-hay frequently contains 3—4 per cent. of lime. Märcker gives the loss of organic matter occasioned by his process as 5.32 per cent.

E. W. P.

**Tobacco Culture.** (*Bied. Centr.*, 1884, 552.)—This paper contains notes relative to the growth of tobacco in Gnadenthal, Switzerland. Three descriptions are cultivated—Virginia, Maryland, and Cuban. It is found that a soil rich in humus gives good results; heavy soils yield greater weight, but inferior quality; newly broken, warm soil produces fine, nicely perfumed leaves. As the roots do not penetrate the soil deeply, the condition of the subsoil is not of much importance. The best manure to use is well rotted, easily assimilable, strong cow-dung; fresh horse and cow-dung make the tobacco sharp, heavy, and biting. Irrigation with liquid manure is also advised. J. F.

**Influence of the Weather on Crops.** By C. FERRARI (*Bied. Centr.*, 1884, 589).—Regarding wheat, rye, and barley, the crop is less the more cloudy are the months March to June, the greater the number of wet days during spring, and the lower the temperature of April to June. From data collected in the valley of the Po, the crop on irrigated rice fields is higher when the skies in July and August are unclouded; maize yields best when the summer is showery. During 1880, and by reason of the cold winter of 1879—80, the crop of grapes was reduced 75 per cent. when the mean winter temperature was  $-40^{\circ}$ , and the reduction is 50 per cent. when the mean temperature is  $-2^{\circ}$ .  
E. W. P.

**Dependence of Cultivation on the Depth of the Soil.** By HEINRICH (*Bied. Centr.*, 1884, 591—593).—Vegetation is largely dependent on the state of concentration of the plant-food in the soil; the fertility of the soil is not at all measured by the total quantity of nourishment present, for a deep soil may contain the same absolute quantity of plant-food as a shallow one, but there the concentration is much lower. Consequently, if there is a want of manure, the soil must be cultivated shallow, so as to keep up the concentration, and deep cultivation without a corresponding increase in manure is prejudicial to the yield; deep cultivation, however, ensures the welfare and certainty of the crop during hard weather, but at the expense of the yield.  
E. W. P.

**Influence of Physical and Chemical Properties of the Soil on Evaporation.** By C. ESER (*Bied. Centr.*, 1884, 505—519).—Although the amount of moisture in the soil depends greatly on meteorological conditions, yet its physical and chemical state exercises much influence, and as this is capable of arbitrary alteration, it is a matter of much practical importance. The author has therefore made an exhaustive series of experiments with soils of various composition, details of which accompany the paper. The general conclusions at which he arrives are as follows:—

The amount of evaporation of a soil depends principally on the amount of water contained when thoroughly wet. All soils appear to yield aqueous vapour at the same rate. Evaporation proceeds so long as the upper layer of soil continues moist, the loss being repaired by capillary attraction from the subjacent layers. When capillary attraction ceases to act, the upper layer dries, and evaporation ceases. This drying diminishes the effects of the ordinary agents of evaporation, wind, &c., and if the upper layer be broken up mechanically it interposes a still deeper shield between the moist subsoil and the drying influences of the atmosphere; the same effect is produced by a top dressing, or covering of the soil. The physical state of the surface is also of great importance, the evaporation from a lumpy coarse surface being considerably greater than from a smooth and well-tilled one, but a too finely powdered soil yields water more readily than that which is in a moderately granular state. Under natural conditions, soil containing humus dries quickest, sand slowest, and clay stands intermediate. The amount of evaporation is greater

in proportion as the surface soil is dark in colour; when there is subsoil-water, the amount of evaporation depends on the thickness and density of the intermediate layers of earth. The position of the ground also affects the question, land exposed to the south losing most. The angle at which ground rises from the level is also important, the loss of moisture being nearly in proportion to the inclination.

J. F.

**Influence of the Soil and its Cultivation on the Temperature of and Moisture in the Air.** (Part I.) By E. WOLLNY (*Bied. Centr.*, 1884, 582—588).—Employing thermometers, the bulbs of which were protected from direct radiation by conical paper shades, suspended at different heights over various classes of soils, the author found that the air over quartz sand was the warmest, followed by dark yellow clay, then chalky sand, and lastly peat; but that the surface of the peat was the warmest, then the quartz sand, clay, and chalky sand. The probable cause for the higher temperature of the peat, whilst the air above it is cooler, is the amount of moisture which it retains, but which, when evaporated, removes much heat. On the other hand, the light-coloured quartz sand reflects much heat; consequently the heat absorbed and employed to evaporate the water is at a minimum, and the heating of the air is the most intense. Chalky sand being light-coloured reflects much heat, but much water is also retained; therefore much heat is retained, and the air temperature falls close to that of the air over the peat. Generalising, we have—soils which are light-coloured and dry communicate most heat to the air, which is reduced when the soil is moist; the minimum of the air temperature is reached when the soil is dark-coloured, and the heat rendered latent by water. Another set of experiments was made on bare soil, and on soil carrying clover, the heights of the thermometer above the surface being 58 cm., 90 cm., and 200 cm., and the results were:—(1) that the air over a field bearing a crop is cooler than it would be were there nothing growing; (2) the variation of temperatures under the first conditions is less than under the second. The first result is brought about by the fact that so much heat is absorbed for the evaporation of the water by the leaves, and direct insolation of the soil is prevented; moreover the absorptive capacity for heat exerted by plants is much higher than that of the stones on the surface. When the plants were moistened, the temperature fell below that of the air above the same class of plant which was kept dry.

To observe the influence of orientation, a pyramid of earth (4 square metres) was constructed, the four faces of which were directed respectively to the four cardinal points, at an angle of 30° to the horizon. As was to be expected, the air over the southern side was the warmest, over the northern side the coldest, whilst the western was warmer than the eastern in the evening, and *vice versa*. E. W. P.

**Result of Removing Débris from the Surface of Sandy Soil.** By E. RAMANN (*Bied. Centr.*, 1884, 594—596).—The soil under observation was sandy, and was covered with the dead needles of pine trees growing on it. A plot from which these needles were regularly removed by a rake was compared with another kept in its natural

state. The second plot was covered with moss and coarse grass, these had been removed from the experimental plot; as regards the moisture present in both plots, it was only in May that the unraked plot was the moister, whilst during June to September the raked plot contained most water down to a depth of 80 cm.; this is because, as the year proceeds, the surface becomes more thickly covered by the leaves which, together with the moss, prevent the penetration of the rain. By keeping the surface of this class of soil bare a considerable loss of mineral matter occurs, by reason of the rain falling on the bare surface, and carrying with it much soluble matter into the lower strata; whilst at the same time decomposition of the silicates proceeds more rapidly than in the covered soil, because of the greater variation of heat and cold. This statement is in opposition to that of other observers on the same subject, but in support of his theory the author states that there is 4·6 per cent. of insoluble minerals in the undisturbed soil, whilst in the raked soil there is 3·6 per cent.; also there is a greater loss of sulphuric acid and potassium. Moreover, as he finds that there is more nitrogen removed in the rubbish than is accounted for by the loss experienced by the soil, he considers that this class of soil can absorb nitrogen from the air; the quantity of total solids removed from the surface is much less than what is lost by solution in the water passing through.

E. W. P.

**Fine and Coarse-grained Superphosphates.** By F. FARSKY (*Bied. Centr.*, 1884, 601—604).—In his earlier communications (*Abstr.*, 1882, 90, 550, 653), Farsky found that sometimes fine-grained, at others coarse-grained superphosphates were most satisfactory. In these experiments, he has attempted to decide the question by experiments made under glass, giving in addition to the superphosphate, sodium nitrate, and watering the plants (buckwheat) once and four times a day; the result thus obtained was in favour of the fine superphosphate and the more frequent watering. In another series, the sodium nitrate was replaced by ammonium sulphate, and the water was given (1) in four equal quantities during the day; (2) one half in the morning, the other half in the afternoon; (3) one quarter morning and three quarters in the evening; (4) the same quantity as in the previous experiment, but given after the soil was much dried. It was found that the regular watering was best on plots manured with the finely divided superphosphate, whilst the irregular watering was more adapted for the coarse-grained manure. On the whole, the finely divided superphosphate is to be recommended for agricultural purposes.

E. W. P.

**Action of Soluble and Insoluble Phosphates.** By A. VOELCKER (*Bied. Centr.*, 1884, 599; *Jour. Roy. Agri. Soc.*, 39, 357).—This is the report of the action of the above manures on the experimental plots at Woburn, during 1880–81–82–83, *i.e.*, during a whole rotation under the four-course system. The report in 1880–81 has already been referred to in a previous volume, and as the clover in 1882 failed, we have only to remark the results obtained in 1883, when the crop was oats. The best yield was obtained on that plot previously manured with Redonda phosphate, which gave the worst results in 1881; dis-

solved and raw bone-meal is advantageous, and the plots produced more than the unmanured plot; the lime plot ranks high, in all probability because of the paucity of lime in the soil (1 per cent.).

E. W. P.

### **Superphosphatic Gypsum as an Absorbent of Ammonia.**

By E. HEIDEN (*Bied. Centr.*, 1884, 606).—Coprolires from Helmstadt and Goslar were treated with sulphuric acid, the resulting soluble phosphate pressed out, and the residue again treated with acid; the residue now consisted of calcium sulphate, with 4—5 per cent. soluble, and 1—2 insoluble phosphate. Compared with other ammonium absorbents as to its action on farmyard manure containing 0.2 per cent. of ammoniacal nitrogen, it was found to be vastly superior.

E. W. P.

### **Employment of Potash Manures in Brittany.**

By G. LECHARTIER (*Compt. rend.*, 99, 658—661).—The crops grown on the reclaimed soils of Brittany after the application of phosphatic manure, rapidly use up the reserve stores of potassium compounds in the soil, and although the granitic rocks from which the soils have been formed contain a notable proportion of potassium, the latter can only be brought into an assimilable form by continual tillage and exposure to the atmosphere. It therefore becomes necessary to employ manures rich in potassium compounds, and the use of such manures is attended with highly beneficial results, especially if they also contain phosphates and nitrogen.

C. H. B.

**Potash Manures for Potatoes.** By MÄRCKER (*Bied. Centr.*, 1884, 607—609).—With the exception of potassium sulphate on good loam, which raised the percentage of starch 3.5 per cent., all other potash manures depressed it 1.5 per cent.; nor was a good result obtained with these manures (kainite, kieserite, &c.) as regards total yield. This statement, however, only applies to spring manuring, for potassium salts, especially on light soils, are necessary for potatoes, but they must be applied at some other period than the spring. The effect of potassium salts on the nitrogen is remarkable; they raise the total nitrogen, but the percentage of albuminoid nitrogen is lowered, the amidonitrogen being correspondingly raised, pointing to the conclusion that the manured tubers were less ripe than the unmanured, but whether this retardation of ripeness was occasioned by the potassium, by the chlorine, or by the magnesia present, is not as yet proved.

E. W. P.

**Sulphuric Acid as Manure.** By F. FARSKY (*Bied. Centr.*, 1884, 642).—A plot manured with a compost to which sulphuric acid had been added, was less productive than another but unmanured plot. This result was probably due to free acid in the compost, as shown by analysis.

E. W. P.



## Analytical Chemistry.

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### Preparation of Standard Solutions of Carbon Bisulphide.

By A. LIVACHE (*Compt. rend.*, 99, 697—698).—When carbon bisulphide is agitated for a short time with a solution of soap in which petroleum has been incorporated by the method previously described (*Compt. rend.*, 97, 249), the bisulphide will dissolve to the extent of 200 grams per litre, although only 150 grams of soap are present, and this solution can be diluted to any extent without precipitating the bisulphide. Resin soaps and various intermediate solvents, such as petroleum, essence of terebenthene, &c., can also be employed, and in this way solutions of different composition, containing definite amounts of carbon bisulphide, can readily be prepared.

C. H. B.

**Estimation of Minute Quantities of Silver.** By C. F. FÖHR (*Chem. News*, 50, 114—115).—For the determination of very small quantities of silver, the author proceeds as follows:—10 grams of substance mixed in the crucible with 20 grams of a mixture of equal parts of flour and potash, are fused with 30 grams of proof lead and salt in a muffle at a bright red heat for about three hours. The lead regulus is scorified once, then cupelled; when it is the size of a poppy seed, it is removed to a fresh cupel for completion, and is finally finished before the blowpipe. The silver bead, which should be perfectly bright and white, is carefully removed, wiped with blotting-paper, and its diameter measured on a scale, which consists of two converging lines, graduated so as to show the amount of silver; the bead is moved along until it touches both lines, and the reading is taken two or three times, with the aid of a lens. By this method a bead may be measured which represents 0.00005 per cent. of silver, when 10 grams of substance are taken.

D. A. L.

**Estimation of Manganese in Cast Iron or Spiegeleisen.** By C. L. BLOXAM (*Chem. News*, 50, 112—113).—The following process is recommended for the determination of manganese in presence of large quantities of iron:—

The metal is dissolved in hydrochloric acid, and after the removal of carbon and silica in the usual way, the solution is heated with a few crystals of potassium chlorate, diluted, nearly neutralised with ammonia, the iron converted into acetate by means of ammonia mixed with excess of acetic acid, and excess of sodium phosphate is then added. The precipitated iron phosphate is separated, redissolved, reprecipitated, &c. The combined filtrates from these two precipitations are mixed with excess of ammonia and boiled (or, better, kept near the boiling point for one hour, and left standing over night). Manganese ammonium phosphate is precipitated, filtered off, washed, ignited, and weighed as pyrophosphate,  $Mn_2P_2O_7$ . Good results are quoted, and compare favourably with some obtained by the bromine method.

D. A. L.

**Volumetric Estimation of Manganese; Influence of Organic Matter and Iron.** By J. B. MACKINTOSH (*Chem. News*, 50, 75).—In reply to a previous communication (Abstr., 1884, 220) of the author, it was suggested (*ibid.*, 499) that the conditions under which he worked were not the same as are encountered in the analysis of spiegeleisen, and on this basis the author's views were contested. In repudiation of this the author has now made seven experiments with spiegeleisen, using the method described in his previous paper (*loc. cit.*), and 0.5 gram for each experiment: in the 1st and 2nd, it was dissolved in hydrochloric acid; in the 3rd, 25 c.c. of standard potassium permanganate was added; in the 4th, 35 c.c. permanganate and a considerable quantity of a mixture of various kinds of organic matter, which were added to the manganese solution after the hydrochloric acid was replaced by nitric acid, the heating being then continued until the organic matter had disappeared; in the 5th, the spiegeleisen was dissolved in nitric acid, the 6th was the same as the 5th, with the addition of organic matter, and in the 7th hydrochloric acid was the solvent, 35 c.c. of permanganate being added without first evaporating off the hydrochloric acid. From the results of these experiments, it is evident that neither the iron nor the carbonaceous matter of the spiegeleisen, nor the extraneous organic matter, have any practical effect on the result; but that hydrochloric acid has the effect of lowering the results, presumably from its action on the manganic oxide; hence it is important that the potassium chlorate employed should be free from chloride.

Expt.	c.c. $K_2Mn_2O_8$ .	Other substances present.	Oxidising power of precipitate, in terms of c.c. permanganate.
1	—	—	13.15
2	—	—	13.15
3	25	—	23.05
4	35	Organic matter .....	26.90
5	—	—	13.15
6	25	Organic matter .....	23.10
7	35	Hydrochloric acid .....	26.55

Expt.	Oxidising power of precipitate less Mn in spiegel taken, in terms of c.c. permanganate.	Theory for $MnO_2$ .	Percentage of theory.
		c.c.	
1	—	—	—
2	—	—	—
3	9.90	10.0	99.0
4	13.75	14.0	98.2
5	—	—	—
6	9.95	10.0	99.5
7	13.40	14.0	95.7

The results were as in Table, p. 85, 0·5 gram of spiegeleisen being taken in each case.  
D. A. L.

**Separation of Arsenic from Antimony and Tin.** By F. HUFSCHMIDT (*Ber.*, 17, 2245—2248).—When experimenting with Bunsen's and with E. Fischer's (*Abstr.*, 1881, 191) methods, the author found that when the arsenic was present in the pentad state, it was very difficult to drive it all over by distillation with hydrochloric acid. He finds, however, that the following modification of this method yields very accurate results.

The solution containing arsenic is made up to about 250 c.c. by the addition of concentrated hydrochloric acid. This liquid is then saturated with hydrochloric acid and distilled, a rapid current of hydrochloric acid being passed through the solution during the whole of the distillation. Almost every trace of arsenic passes over in the first 50 c.c. of distillate, but for perfect safety the author advises the collection of about 100 c.c. of distillate. The results are equally good with arsenic as with arsenious salts. The very volatile arsenious chloride formed should be condensed by passing into a Woulff bottle containing potash. No trace of tin or antimony is volatilised. The author gives numerous test estimations of arsenic, both alone and in the presence of antimony and tin, the results being very close and concordant. The arsenic found was almost always within 0·3 per cent. of that employed, when from 0·07 to 0·15 gram arsenic was used.  
L. T. T.

**Examination of Water.** By R. ANGUS SMITH (*Second Report* (1883) *to the Local Government Board as Inspector under the Rivers Pollution Prevention Act*).—This posthumous report consists of an inquiry into certain characteristics of potable and other waters, and especially of new methods proposed by the author for examining the organic substances found in them which are of such a character as may be supposed to affect health. The first, which promised to be the most important, indicates a method for measuring the amount of organic activity, or animal or vegetable vitality, amongst the microbes (at least of a certain class) which exist in the waters. The second part of the report continues the proof, formerly given in the author's first report (1882), of the natural purification of rivers, now, in his opinion, beyond dispute, as it can be shown in the laboratory. The third part is an account of a method for examining water by means of Koch's gelatin process. This part the author considered to be only partly worked out, but its general character, he says, may be seen, and the novelty of photographic proofs is a valuable addition to ordinary chemical analysis.

Part I. *The Hydrogen Process*.—This process depends on the fact that most natural waters when treated with sugar and allowed to stand, after a certain time give off hydrogen gas. The formation of hydrogen during the decomposition of sugar by vibrios has already been observed, and also its formation in very small quantities from organic matter in some decompositions. The author, however, was unaware that Heinsch, who first used sugar as a

test for water, observed that hydrogen gas was liberated, and he therefore has brought forward the action of sugar on the organic matter in water, as a method for measuring the amount of organic life existing in the water, by means which may be considered as purely chemical. The following is a description of the process.

Tubes  $7\frac{1}{4}$  inches long,  $\frac{3}{8}$  inch diameter, and holding 50 c.c., were filled with the water to be examined, and 1 per cent. of grape-sugar was added. These tubes were then inverted, sealed at the bottom with mercury, and allowed to stand for some weeks. If the purest distilled water be used no gas is evolved, nor is gas evolved if the natural water be first boiled. From most of the waters experimented with, gases commenced to collect in five days, and for purposes of comparison, the gases were collected and analysed after 21 days in the whole series of results given in this report. The total amount of gas obtained in that time varied from 0 c.c. to 14 c.c. The amount of gas remaining dissolved in the water after the evolution in the cold was not considered, but it was the author's intention to have included this in his investigations. The presence of carbonic anhydride was proved by absorption with caustic potash, the absence of oxygen by pyrogallol, and the presence of hydrogen by adding oxygen and exploding the mixture. The residue was found to be nitrogen. The presence of carbonic anhydride was to be expected, the author before analysis having presumed that all the gas evolved was carbonic anhydride. Nitrogen had come partly from the nitrogenous compounds decomposed, and partly from nitrogen in solution, and it also was the author's intention to have investigated this decomposition. The question considered in this report is the production of hydrogen, and as neither carbonic anhydride nor nitrogen has ever appeared in such cases without hydrogen, the author considers that gas to be the characteristic of the decomposition.

The results of the analysis of the gases evolved from a large number of waters collected from various parts of the country are given in full. They are grouped in 21 tables, of which the following are examples:—

TABLE 11.—*London Waters; received May 8, 1883. Sugar alone added.*

	c.c. of gas evolved from 50 c.c. of water.	c.c. of hydrogen evolved from 50 c.c. of water.	c.c. of nitrogen evolved from 50 c.c. of water.	c.c. of carbonic anhydride evolved from 50 c.c. of water.	Percentage composition of gases.		
					Hydrogen.	Nitrogen.	Carbonic anhydride.
A	7·09	4·40	0·93	1·76	62·04	13·16	24·80
B	5·75	3·74	1·40	0·61	65·00	24·44	10·56
C	8·31	5·47	2·07	0·77	63·21	24·90	9·24

TABLE 12.—*London Waters; received May 8, 1883. Sugar and Sodium Phosphate added.*

	c.c. of gas evolved from 50 c.c. of water.	c.c. of hydrogen evolved from 50 c.c. of water.	c.c. of nitrogen evolved from 50 c.c. of water.	c.c. of carbonic anhydride evolved from 50 c.c. of water.	Percentage composition of gases.		
					Hydrogen.	Nitrogen.	Carbonic anhydride.
A	6·31	3·82	0·93	1·56	60·34	14·85	24·81
B	4·20	2·72	0·63	0·85	64·80	14·89	20·31
C	9·00	5·19	1·63	2·18	57·65	18·14	24·21

TABLE 13.—*London Waters; received May 8, 1883.*

The waters were previously softened by Clarke's process, then sugar and sodium phosphate were added.

A	3·00	1·86	0·84	0·30	65·21	24·84	9·95
B	4·50	2·91	1·14	0·45	64·72	25·28	10·00
C	7·50	4·22	1·78	1·50	56·24	23·74	20·02

TABLE 14.—*London Waters; received May 8, 1883.*

The waters were allowed to stand for 48 hours, and to the deposit sugar and sodium phosphate were added.

A	10·37	6·66	2·32	1·39	64·21	22·34	13·45
B	8·24	3·46	3·62	1·16	60·20	25·68	14·12
C	6·78	4·40	1·62	0·76	64·93	23·86	11·21

TABLE 15.—*Waters from Lancashire and its Borders; collected Oct. 5, 1883. Sugar alone added.*

A	4·50	3·04	0·42	1·04	67·55	9·33	23·12
B	4·13	3·11	0·45	0·57	75·30	10·89	13·81
C	10·00	7·57	0·75	1·68	75·70	7·50	16·80
D	12·13	9·46	1·10	1·57	78·00	9·06	12·94
E	21·00	16·80	1·24	2·96	80·00	5·90	14·09
F	0·00	0·00	0·00	0·00	0·00	0·00	0·00
G	0·00	0·00	0·00	0·00	0·00	0·00	0·00
H	0·00	0·00	0·00	0·00	0·00	0·00	0·00
I	8·63	0·00	0·87	1·26	75·31	10·08	14·61
J	0·00	0·00	0·00	0·00	0·00	0·00	0·00
K	0·00	0·00	0·00	0·00	0·00	0·00	0·00
L	14·00	11·11	1·21	1·68	79·37	8·64	12·00

The names of the London water companies to which the letters A, B, and C refer are omitted in the report. The letters in Table 15 refer to the following samples:—

- A. Fountain below Hadfield, Woodhead.
- B. Paradise Well, village of Tintwhistle.
- C. 1st Reservoir, Tintwhistle.
- D. 2nd Reservoir.
- E. Scum from 2nd Reservoir.
- F. Stream, mountain side, between Tintwhistle and Woodhead.
- G. Mountain stream.
- H. Mountain stream, near Crowden Station.
- I. 3rd Reservoir.
- J. Mountain stream, near Woodhead.
- K. Mountain stream, 1 mile from Woodhead Station.
- L. 5th Reservoir.

The following table gives the average amount of hydrogen from all the waters examined, and the number of samples in each table:—

	Average amount of hydrogen evolved in c.c. from 50 c.c. water.	Number of samples.
Derbyshire waters (Buxton and neighbourhood), April 19th, 1883—		
Sugar alone added to the waters .....	1·09	9
Sugar and sodium phosphate added.....	1·56	9
Flintshire waters (Mostyn, Holywell, St. Asaph)—		
Sugar alone added to the waters .....	1·95	7
Sugar and sodium phosphate added.....	2·01	7
London waters; received Feb. 13th, 1883—		
Sugar alone added to the waters .....	2·69	5
Sugar and sodium phosphate added.....	2·59	6
London waters; received April 12th, 1883—		
Sugar alone added to the waters .....	2·85	5
Sugar and sodium phosphate added.....	3·20	5
The waters were allowed to stand for 48 hours: then the clear water was syphoned off, and sugar added to the clear water .....	2·54	5
The waters were allowed to stand for 48 hours: then the clear water was syphoned off, and sugar added to the deposit.....	3·57	5
London waters; received May 8th, 1883—		
Table 11 (see page 87) .....	4·54	3
Table 12 (    "    88) .....	3·91	3
Table 13 (    "    88) .....	3·00	3
Table 14 (    "    88) .....	4·84	3
Lancashire waters; collected October, 1883—		
Table 15 .....	3·71	11
Sewage rivers: Irk, Irwell, Medlock, and canal waters—		
With sugar added .....	8·88	10

	Average amount of hydrogen evolved in c.c. from 50 c.c. water.	Number of samples.
Salford sewage water— With sugar added .....	5.04	4
Scum from reservoir at Woodhead .....	16.80	1
Mud from a stream at Buxton— Sugar alone added .....	4.49	1
Sugar and sodium phosphate added.....	5.53	1

The author considered his results—when it is remembered that they are first experiments of a very delicate nature—as fairly uniform, although in certain instances unexpected results were obtained. From the analyses it is found that the higher waters in Derbyshire give out less hydrogen than the lower waters where sewage enters the brooks, and also give out less gas than the lower waters of the drainage of the Thames Valley, or any other place. The waters of Longdendale and neighbourhood, which form the supply of Manchester, as a rule are very free from hydrogen, and in some trials of Manchester water no hydrogen was obtained, showing the great purity at times of the water so far as this test is capable of illustrating it.

A series of experiments was also made to test the effect of bacteria on the evolution of hydrogen, and to find if they were the actual cause of the evolution. The microbes used were obtained from the surface of gelatin which had been dissolved in water containing more or less sewage, and allowed to stand for a time. The liquid portion at the surface contained countless numbers of bacteria; and in each case a small drop was all that was required. The results showed (for full particulars the original paper must be consulted) that Medlock water which contains sewage and chemicals, gave out its hydrogen much more quickly when bacteria were added: that the addition of bacteria to distilled water produces results such as are found in less pure water; that Manchester water when boiled and thus rendered incapable of producing gas from sugar, gave out hydrogen when bacteria were added; and that by adding more sugar and bacteria to a water which had given out a great deal of hydrogen, gases consisting of hydrogen and carbonic anhydride, with little or no nitrogen, were again evolved.

The author, in discussing the value of this method, considered that in many natural waters sugar is made to ferment and give out hydrogen gas, and that the amount of this gas, which in some is very small, increases in proportion to the impurity in the water. That the kind of microbes is such, that if present in large numbers they render the water impure to the senses, and that decompo-

sition is caused by organisms in this way is shown by the absence of hydrogen on treating boiled water by sugar.

That this method of estimation deals with bodies of an offensive character we have the fact of their increase from the purest water of the mountain to the worst sewage. As far as the hydrogen is concerned, there seems to be a regular gradation. According to Pasteur, it appears that microzymes may be various in activity without changing their appearance, that they may be attenuated to any extent, and that their power may be virulent to any extent. To say that a certain class of microbes is present is not to have a very definite idea, the importance lies in the activity. The author could not say whether this method is a real measurement of the amount of organic life, or only a measurement of the vitality of certain organisms, but if microbes when very active decompose sugar and produce hydrogen in greater abundance than when inactive, then the hydrogen becomes the measure of their power.

The author has further discussed and speculated as to the value of this method at great length, but finally says that whether it measures the activity, quantity, or other characteristics of the organisms in the water, is a matter yet to be decided.

Part II. *The Elimination of Nitrogen during Putrefaction of Water.*—This is a continuation of the author's work published in his first report on water (1882). From the first report he quotes largely, and has shown (1) that bodies containing protein compounds when in abundance of water and in common air may be oxidised and form nitric acid; (2) that the same organic bodies in a state of decomposition, and in water, may be oxidised at the expense of the nitrates, and give off nitrogen. In the first case, a certain quantity of sewage is in the water, but is overpowered by the air, in the second the sewage is in excess, and overpowers the nitrates. He has shown also that the purification of sewer river water is effected in nature first by putrefaction, and secondly by thorough oxidation. He gives some further results which show the escape of free nitrogen from sewer river water when treated with potassium nitrate.

(1.) 1150 c.c. of Medlock water when treated with 1 gram of nitre gave off 103.3 c.c. nitrogen in 39 days (1 gram potassium nitrate contains 110.2 c.c. nitrogen).

(2.) Bridgewater Canal water and Manchester water, when treated with potassium nitrate, gave off no nitrogen after 46 days' observation.

(3.) Salford sewage water when treated with 0.1 per cent. of nitre gave off the whole of the nitrogen contained in the potassium nitrate, in 22 to 28 days; in some cases a little more was given off afterwards.

The remainder of this part contains Lauth's results (*Compt. rend.*, 84, 417) on the same subject.

Part III. *The Gelatin Process.*—The use of gelatin as an indicator of the amount of vital matter in water was suggested by Koch's work. The chief advantage in the method is that the gelatin prevents the water from moving, and that every point which has vitality in it is able to assert itself, the number existing in the water being seen at a glance. The following is the method employed by the author:—

A solution containing 5 per cent. of solid thin leaf gelatin was



heated to 100°, clarified with fresh albumin, and filtered. This solution melts at about 27°. 25 c.c. of this solution, at a little over 27°, were mixed with 25 c.c. water in a test-tube, about 8 inches long and 1 inch diameter, closed with a stopper of cotton-wool, and kept for a few minutes at 27°. Along with the waters to be tested, distilled water and Manchester water were thus treated for the sake of comparison. The rest of the process consists in observing day by day the changes in the gelatin. The number of spheres or centres of microbes is one measure, the depth to which the surface becomes liquid is a second, and the number of days before putrescence sets in is a third. In the case of most waters, the gelatin is completely decomposed in about 7 days, but much depends on the temperature, and in the case of pure distilled water it may keep for a much longer time; a photograph of a gelatin solution with distilled water is shown which at the end of 15 days is still quite undecomposed.

The results seem to show that in sewer waters, and in very impure waters, the gelatin is rendered liquid at the surface, and this fluidity increases until the whole becomes liquid. The liquid is alive with bacteria. In the case of potable waters, such as the Manchester water, the whole tube becomes in two or three days filled with perfectly formed transparent spheres at the bottom of which is a little white line. These are found to be liquid and to contain a great mass of active and inactive bacteria. Also a number of minute white specks appear which seem to indicate the number of points of vitality; they are also filled with bacteria, but of a different kind, as they do not form liquid spheres around them. In some cases, gases are evolved, and form globules or discs in the gelatin. The effects, or rate of effects, depends much on the temperature, and, without comparison with known waters, conclusions should not be drawn.

Of all the forms of change, that which seems to be connected with the most offensive water, is the liquefying of the surface. The other changes are more or less objectionable, according to the number of points of activity which the author considers are measures of impurity. Whether these germs are to be supposed as productive of disease, or productive of it by their multiplication, the author was unable to say, but in those cases where they are most numerous, the water is not so good to the senses, and therefore the method is clearly an independent measure of excellence.

The hydrogen method agreed well with the results obtained with gelatin, but the gelatin sometimes showed minute impurities when hydrogen did not appear. Whether the microbes which transform gelatin also produce hydrogen, the author was unable to decide, but as the results correspond very fairly, the probability is in favour of the affirmative.

The author had prepared photographs of 125 samples of water treated with gelatin (in some cases with sugar, or sodium phosphate, or both, in addition), and has minutely described many of them. Unfortunately the whole of the photographs could not be included in the report, but those selected by the author are very good examples of the appearance of the gelatin after 3, 5, or 7 days. A few of them are comparable. The photographs of a series of London waters with

gelatin may be compared with those of a series of Derbyshire and Flintshire waters—the London waters seem to be inferior to the others. Manchester water was always found superior by this test to London water. For the description of the changes, the original paper and the photographs themselves must be referred to. The following is a description of a few :—

October, 1883.—Distilled water: No alteration during 8 days' observation.

Manchester water (from laboratory tap): After 3 days, innumerable small spheres appeared. After 4 days, these spheres had increased in size, the surface of the gelatin remaining firm. After 5 days, a deposit had formed at the bottom of the spheres, and transformation of the gelatin was taking place very rapidly.

Samples of water taken from the reservoirs for the supply of Manchester, between Woodhead and Hatfield, gave similar results to the Manchester tap water. Samples of water, taken from the mountain sides at Woodhead, developed a large number of "points" after 3 days. After 4 days, discs of gas appeared, but spheres were absent. "Dots" or small "specks" were observed, but they did not increase in size.

Scum taken from one of the reservoirs showed after three days innumerable dots dispersed throughout the gelatin, and a large number of discs of gas also appeared. The gelatin gradually softened, and the development of the germs was far more advanced than in any of the other specimens of water under examination.

April 20th, 1883.—Distilled water: No alteration after 15 days' observation.

Manchester water: On the second day a number of minute spheres appeared, which had enlarged on the third day, the surface of the gelatin being unaltered. On the fourth day the spheres had increased in size and number, and a deposit was forming at the bottom of the spheres.

Water from below Buxton receiving sewage, although looking clear: On the second day, a distinct band of minute spheres appeared at the surface of the gelatin. On the third day, the surface of the gelatin was quite liquid to a depth of 5 mm., and of a greenish colour. On the fourth day, a few discs of gas appeared, the surface of the gelatin being liquid to a depth of 7 mm.

In the same way, London water collected from the various companies' supply in February, April, and May, 1883, are described by the aid of photographs, and compared with distilled and Manchester water.

A. B.

**Testing Mineral Oils.** By E. VALENTA (*Dingl. polyt. J.*, 253, 418—421).—Referring to the adulteration of mineral oils with resin oils the author, in a previous communication (Abstr., 1884, 1079) mentioned that by the aid of glacial acetic acid at a certain temperature, it is possible to detect adulterations of mineral oils with resin oils with comparative ease. He has continued his researches in this direction, and now gives the results of some experiments which he has obtained in conjunction with Feigerle.

*Solubility Values of Different Mineral Oils. Sp. gr. of Glacial Acetic Acid at 15° = 1.0562.*

No.	Name of mineral oil.	Sp. gr. at 15°.	Oil dissolved by 100 grams glacial acetic acid at 50°.	Oil dissolved by 10 c.c. glacial acetic acid at 50°.	Remarks.
			grams.	grams.	
1	Lubricating oil	0.9090	5.7648	0.6089	Pale yellow, clear, highly fluorescent oil, almost colourless.
2	Ditto .....	0.9090	5.7789	0.6104	
3	Engine oil (yellow)	0.9139	5.7333	0.6056	Dark orange colour, odourless, highly fluorescent, and clear.
4	Machine oil (yellow)	0.9109	4.7778	0.5046	Pale yellow, highly fluorescent, and odourless.
5	Heavy mineral oil (thin)	0.9090	4.2810	0.4522	Oils having a pale yellow to orange-yellow colour, fluorescent, perfectly neutral, and odourless.
6	Light mineral oil (thin)	0.8880	4.7009	0.4965	
7	Fatty mineral oil (thick)	0.9070	2.6729	0.2823	
8	Green oil ....	0.9105	6.4988	0.6849	Blackish - brown non-transparent oil, having a tarry odour.
9	Blue oil .....	0.9016	6.0170	0.6342	Dark brownish - red, opaque, highly fluorescent, tarry odour.
10	Vulcan oil ....	0.9259	3.3451	0.3525	Almost black - brown, opaque, thin liquid oil, tarry odour, highly fluorescent.

For quantitative estimation, the method adopted is as follows :— 2 c.c. of the oil are treated with 10 c.c. glacial acetic acid, and heated for five minutes in a loosely corked test-tube in a water-bath. The mixture is then passed through a small filter, and the middle part of the filtrate collected. A weighed quantity of this solution is titrated with standard alkali and the weight of glacial acetic acid contained in the solution calculated. The difference in the weight between the solution and the glacial acetic acid gives the amount of oil contained in the former. It has been found, however, by experiment that the solubility does not increase with the percentage of resin oil contained in a mineral oil, hence this method is not suitable for the quantitative determination of the amount of resin oil in such mixtures. The sub-joined table gives the numbers which were obtained for the solubility of different mixtures of oils containing a known amount of resin oil.

*Solubility of Different Mixtures of Yellow Engine Oil and Crude Resin Oil at 50°. Sp. gr. at 15°: Glacial Acetic Acid = 1.0562, Mineral Oil = 0.9139, and Resin Oil = 1.0023.*

Amount of resin oil in the mixture.	Oil dissolved by 100 grams glacial acetic acid.	Oil dissolved by 10 c.c. glacial acetic acid.	Remarks.
Per cent. by vol.	grams.	grams.	
0	5.7333	0.6056	The crude resin oil was obtained from Wagenmann, of Vienna. It had a dark brown colour, tarry odour, high viscosity, and resinified in the air.
25	7.3973	0.7796	
50	8.3653	0.8816	
75	12.5601	1.3237	
100	16.8782	1.7788	

The rotatory power of resin oils may be employed for the recognition of the purity of a mineral oil, the latter being optically inactive. For this purpose, the author recommends the use of Mitscherlich's polarising apparatus, with the modification that in the case of highly coloured oils, they are first subjected to a treatment with potassium ferrocyanide and filtered. A further difference between resin and mineral oils is their behaviour with iodine. The author adopted the method recently described by Hübl (*ibid.*, 253, 284), and found that mineral oils fail to absorb more than 140 mgrms. iodine per gram of oil, whilst the iodine number for resin oils ranged between 430 and 480 mgrms. D. B.

**Determination of the Nature of the Crude Oil in Turkey-red Oil.** By A. MÜLLER-JACOBS (*Dingl. polyt. J.*, 253, 473).—On rendering a very dilute solution of Turkey-red oil alkaline with aqueous ammonia, the mixture should remain perfectly clear on standing. The formation of a precipitate indicates the presence of solid fats or their corresponding natural glycerol ethers (palmitin and stearin), and shows that for the manufacture of the Turkey-red oil either impure castor oil or other crude oils, such as rape oil, sesamé oil, train oil, cotton-seed oil, olive oil, or mixtures of both were used. The separation takes place only in very weak solutions, in which the solvent action of sodium sulpholeate fails to prevent the precipitation of the solid fats.

To recognise the purity of Turkey-red oil, Beusemann recommends the determination of the melting point of the fatty acids separated therefrom. On decomposing Turkey-red oil by boiling it with dilute acids, and determining the melting point of the resulting mass, which consists of unaltered oil and liquid and solid acids, it is possible also to judge of the nature of the crude oil employed in the manufacture. Finally, the behaviour of the separated mass with alcohol affords valuable indications of the purity of Turkey-red oil; that from the pure oil, obtained from castor oil, forming a clear solution, whilst the mass separated from other crude oils gives a turbid solution with

alcohol, and this, on standing, deposits oily particles consisting of unaltered triglycerides. D. B.

### Bromine as a Test for Quinine, Narcotine, and Morphine.

By A. EILOART (*Chem. News*, 50, 102—103).—The following note refers to the delicacy of various modes of employing bromine for the detection of certain alkaloids. *Quinine*.— $\frac{1}{50000}$  part can be detected in solution by the red colour produced by the successive addition of bromine water, mercuric cyanide, and precipitated chalk;  $\frac{1}{80000}$  by using bromine water, potassium ferrocyanide, and borax, Vogel's test;  $\frac{1}{80000}$  by employing petroleum instead of mercuric cyanide, or with Bloxam's test (Abstr., 1883, 1175), when chalk is added before the bromine, or by the green fluorescence produced when a neutral solution of quinine is mixed with excess of bromine, boiled to expel the excess, and then cooled;  $\frac{1}{15000}$  when bromine (without debrominating agent) and chalk are used; in such cases, neutralising agents, weak ammonia, zinc oxide, &c., produce a crimson colour;  $\frac{1}{15000}$  can also be detected with Bloxam's test, as described (*loc. cit.*). *Narcotine*.— $\frac{1}{60000}$  part gives a red colour if its hydrochloric acid solution, containing a slight excess of bromine, is neutralised with calcium carbonate; with more than  $\frac{1}{10000}$  of narcotine, the red is followed by violet and blue. This is the case even after the solution has been brominated for some time, whereas quinine gives no colour with chalk after standing. Tartaric or acetic acid impedes the production of the colour. *Morphine*.— $\frac{1}{12000}$  part produces a red colour, when a solution containing it is boiled with excess of bromine water, neutralised with chalk, and again boiled; smaller quantities give rise to an orange or brown coloration, which is bleached by bromine water;  $\frac{1}{120000}$  can be detected by the bleaching effect of bromine water on the subdivided neutralised solution. *Strychnine*, *cinchonine*, and *cafféine* give no characteristic reaction with bromine and chalk. D. A. L.

### Estimation of the Wool, Silk, and Cotton in Tissues.

By A. REMONT (*Chem. News*, 50, 123—124).—Four portions of the material to be examined are taken, each weighing 2 grams. One is reserved, the other three are boiled for a quarter of an hour in 3 per cent. hydrochloric acid, and if the liquid is very much coloured the boiling is continued for half an hour longer with fresh acid; this operation removes the dressing; one of these three samples is reserved. To remove the silk from the other two, they are dipped for one or two minutes into a boiling solution of basic zinc chloride (60° B.), which is prepared by heating a mixture of 1000 parts of fused zinc chloride, 850 parts of water, and 40 parts zinc oxide, until the latter is dissolved. The two samples are then washed, first in acidulated and then in pure water; one is reserved, the other is *gently* boiled for a quarter of an hour in 60 to 80 c.c. of soda solution (sp. gr. 1.020) to remove wool; the residue is washed as in the last case.

The four samples are now heated in distilled water for a quarter of an hour, left to dry spontaneously, and are then weighed. The first should weigh 2 grams, if it does not, any considerable loss must be taken into account, the difference between the weights of samples 1

and 2 is the weight of the dressing, between 2 and 3 that of the silk, between 3 and 4 the wool, the residue being the vegetable fibre; the last two are only approximate, as the vegetable fibre is somewhat attacked by the soda solution.

Boiling with dilute acid removes dyes readily from cotton, less readily from wool, and only imperfectly from silk. Dark-coloured silks are most heavily weighted, and sometimes the weighting is so heavy that the colour is not sufficiently removed; it is then necessary to determine the amount of iron present in the ash of a few threads of the treated sample, and if it exceeds 5 per cent., it must be taken into account.

D. A. L.

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## Technical Chemistry.

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**Antiseptic Properties of Carbon Bisulphide.** By CKIANDI-BEY (*Compt. rend.*, **99**, 509—511).—Carbon bisulphide is soluble in water to the extent of from 2 to 3 parts per million at 18—20°. By agitating carbon bisulphide with water in a flask completely filled, a solution can be obtained containing approximately as much as 0·5 gram of carbon bisulphide per litre. Carbon bisulphide alone and in aqueous solution arrests all fermentations, kills microbes, and is one of the most energetic of antiseptics. It moreover possesses considerable penetrating power. A solution of carbon bisulphide in alcohol of 96° decomposes slowly and gives rise to various products, notably hydrogen sulphide.

During 20 years' experience amongst workmen continually exposed to the vapours of carbon bisulphide, the author has never observed any paralysis of lower or upper limbs, nor any destruction of masculine faculties. When breathed in certain proportions, the vapour of carbon bisulphide produces effects similar to those of etherisation, the only disagreeable after-effect being heaviness of the head, which soon passes off. When applied to the skin, carbon bisulphide acts almost instantly as an energetic revulsive, the pain produced being similar to that caused by boiling water. The pain, however, ceases as soon as the carbon bisulphide is volatilised, and no ulceration is produced.

The author recommends the use of carbon bisulphide both externally and internally, in aqueous solution and in the form of spray, in cases of cholera, typhoid, and other diseases resulting from the action of microbes. It may also be used to disinfect the evacuations, clothes, &c., of cholera patients and others, and an aqueous solution may be employed to water the streets and to wash out rooms in cases of epidemics. Dr. Dujardin-Baumetz finds that the internal administration of an aqueous solution in cases of typhus arrests the diarrhoea, and disinfects the breath and the excretions of the patient.

When the aqueous solution is swallowed, it has a sweet, warm taste,  
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and produces a sensation of warmth in the stomach, followed after some time by irritation of the nose similar to that produced by sulphurous anhydride. These sensations are followed by slight heaviness of the head, which soon passes away.

For medicinal use, the carbon bisulphide must be carefully purified by agitating it with mercury until no further formation of mercuric sulphide takes place.

C. H. B.

**Preparation of Potassium Magnesium Sulphate.** (*Dingl. polyt. J.*, 254, 48.)—The *Consolidirten Alkaliwerke* of Westeregeln first prepare the crude salt as artificial carnallite, which is then decomposed by treatment with schönite mother-liquor. By this treatment, the amount of potassium chloride is doubled, whilst the mother-liquor becomes proportionally richer in magnesium chloride. The product is then warmed with a corresponding amount of magnesium sulphate solution. On cooling, schönite, amounting to 65–70 per cent. of the potassium chloride employed, separates out, the rest remaining in solution, which is applied as above, to decompose the artificial carnallite. The solution can be evaporated so that artificial carnallite crystallises out, or it may be employed as solvent for crude salt.

J. T.

**Manufacture of Aluminium.** (*Dingl. polyt. J.*, 253, 426.)—Gadsden (Ger. Pat. 27,572, August, 1883) proposes to prepare aluminium by subjecting aluminium chloride to the vapour of sodium evolved from retorts in which a mixture of sodium carbonate with charcoal is intensely heated.

For the manufacture of aluminium-bronze, Webster (Ger. Pat. 28,117, January, 1884) prepares (1) an alloy consisting of 15 parts aluminium and 85 parts tin, and (2) an alloy composed of 17 parts nickel, 17 parts copper, and 66 parts tin. He then fuses equal parts of these alloys with copper, the best result being obtained with 84 parts copper to 8 parts of each alloy. The resulting bronze is suitable for the preparation of castings of various kinds, tubes, guns, plates, wires, hydraulic apparatus, boiler-plates, domestic utensils, &c.

D. B.

**Utilisation of Zinciferous Burnt Pyrites.** (*Dingl. polyt. J.*, 254, 89–90.)—The mining and smelting directors of Königshütte propose to roast burnt pyrites containing zinc with sodium chloride, and then to extract with water acidified with hydrochloric acid. The solution is freed from copper when necessary, and freed from sodium sulphate by concentration and cooling. The zinc solution is then treated for metallic zinc or for zinc preparations, by known methods.

J. T.

**The Siemens-Martin Process.** By M. JUNGCK (*Dingl. polyt. J.*, 253, 509–514).—The author gives a detailed account of the mode of working this process at the Phoenix Iron Works in Ruhrort. The gas generator consists of eight chambers, which are charged at intervals of three hours with about 600 kilos. of coal having the following composition:—



Carbon.	Hydrogen.	Oxygen and nitrogen.	Ash.
71.10	4.24	11.92	12.74

The gas from two chambers is sufficient for the working of one reverberatory furnace. Each furnace is provided with four regenerating chambers. The charge consists of about 400 kilos. grey pig iron, 150 kilos. spiegeleisen, 1500 kilos. steel scrap, and 25 to 50 kilos. wrought-iron scrap, from 20—40 kilos. spiegeleisen being added towards the end of the heating. A charge is worked off in from 8—9 hours. The author has investigated the working of a charge consisting of spiegeleisen, English grey pig iron (Maryport), and Bessemer pig iron, which was produced at the Phoenix Works. The pig iron used had the following composition:—

	Graphite.	Combined carbon.	Mn.	Si.	P.
Bessemer pig iron ..	3.09	0.97	2.55	1.59	0.116
English pig iron ....	3.45	0.71	0.12	2.37	0.059

	Cu.	S.	Fe.
Bessemer pig iron ....	0.249	0.018	91.417
English pig iron ....	trace	trace	93.291

After fusing this mixture, some ends of Bessemer steel rails were added, and finally spiegeleisen. The steel when tested was found to fulfil the requirements of good Martin steel. It gave by analysis—

Mn.	C.	Si.	P.	S.	Fe.
0.304	0.336	0.035	0.160	0.006	99.159

The slag had the following composition:—

SiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	S.	FeO.	Al <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.
50.18	0.02	0.014	25.75	2.61	20.44	0.62	0.17

The author then describes a second process, in which the furnace was worked too cold. The steel produced was too soft, and had to be reworked with an additional quantity of spiegeleisen until the desired degree of hardness was obtained.

The following analysis gives the composition of the gas from the generator, tested in accordance with Stöckmann's method:—

	Per cent. by volume.	Per cent. by weight.
Nitrogen .....	61.49	64.83
Carbonic anhydride .....	4.45	7.36
Carbonic oxide .....	23.24	24.50
Hydrocarbons .....	2.07	1.24
Hydrogen .....	6.49	0.55
Steam .....	2.26	1.52

The gas contained 13.61 per cent. (by weight) of lamp-black and

ash, and 0.9 per cent. tar. Since, in addition to the 13.61 per cent. of soot and ash, only about 27 per cent. of calorific substances were contained in the gas, the decrease of the temperature in the furnace is easily explained. D. B.

**Analysis of some Indian Bronzes and their Patina.** By A. ARCHE and C. HASSACK (*Dingl. polyt. J.*, **253**, 514—519).—The investigation which forms the subject of the present paper refers to two Indo-Chinese ceremonial drums, placed at the disposal of the authors by Count Hans Wilczek. One of these was recently bought for the Natural History Museum of Vienna, whilst the other belongs to Count Wilczek, and was shown at the Bronze Exhibition in Austria in 1883. The first drum (marked A) is perfectly sound, but the second drum (marked B) has lost its pedestal, and has been repaired with bronze plates in one or two defective places, otherwise both instruments are similar in form, size, and design. It was found that the pieces used for repairing the drum B did not belong to the missing pedestal, as their composition differed considerably from that of the metal B. The authors therefore subjected this patchwork to a separate examination, so that three Indian bronzes and their patina were analysed.

Analysis of the three alloys:—

	Cu.	Pb.	Sn.	Sb.	As.	Fe.	CaO.	SiO <sub>2</sub> .
A.....	60.82	15.68	10.88	1.16	traces	0.91	0.38	1.13
B.....	70.79	14.25	4.90	3.21	0.79	0.30	0.12	1.26
Patchwork	68.78	17.55	6.88	—	—	0.85	traces	0.29

	S.	C.	H <sub>2</sub> O.	O.
A.....	1.37	1.05	2.92	3.13 = 99.43
B.....	2.20	0.94	0.89	— = 99.65
Patchwork..	1.49	0.70	1.89	0.66 = 99.09

The patchwork had been fastened with iron rivets. Small pieces of solder were detected also. The iron rivets gave by analysis iron 97.43, carbon 2.20, and traces of sulphur and phosphorus. The solder was composed of—

Cu.	Pb.	Sn.	Zn.	Fe.	SiO <sub>2</sub> .	As, S, Co, Ni.	H <sub>2</sub> O, CO <sub>2</sub> , loss.
66.70	3.78	0.55	23.97	0.82	0.12	traces	4.06

Analysis of the patina:—

	CuO.	PbO.	SnO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	SiO <sub>2</sub> .
A.....	28.08	4.95	0.45	2.82	1.19	traces	45.29
B.....	11.00	0.59	0.05	1.11	0.31	traces	77.51
Patchwork	26.11	12.93	10.52	4.46	5.66	0.27	15.24

	SO <sub>3</sub> .	CO <sub>2</sub> .	C.	Water of hydration.	Water.
A.....	traces	6.33	2.16	4.27	3.92 = 99.46
B.....	traces	1.60	0.75	1.90	3.18 = 98.00
Patchwork	0.97	5.14	3.88	6.15	7.04 = 98.42

**Patina A.** The numbers obtained by analysis agree with the formulæ  $\text{CuCO}_3, 2\text{CuO}_2\text{H}_2$  and  $2\text{PbCO}_3, \text{PbO}_2\text{H}_2$  :—

28.08 CuO require for $\text{CuCO}_3, 2\text{CuO}_2\text{H}_2$ . . . .	5.35 $\text{CO}_2$ .
4.95 PbO                   ,, $2\text{PbCO}_3, \text{PbO}_2\text{H}_2$ . . . .	0.65   ,,
Total. . . . .	6.00   ,,
Found . . . .	6.33   ,,

**Patina B** contains a copper carbonate poorer in carbonic anhydride and the same lead carbonate as patina A :—

11.00 CuO require for $\text{CuCO}_3, 3\text{CuO}_2\text{H}_2$ . . . .	1.53 $\text{CO}_2$ .
0.59 PbO                   ,, $2\text{PbCO}_3, \text{PbO}_2\text{H}_2$ . . . .	0.08   ,,
Total. . . . .	1.61   ,,
Found . . . .	1.60   ,,

The patina of the patchwork contains the same carbonates as B :—

26.11 CuO require for $\text{CuCO}_3, 3\text{CuO}_2\text{H}_2$ . . . .	3.63 $\text{CO}_2$ .
12.98 PbO                   ,, $2\text{PbCO}_3, \text{PbO}_2\text{H}_2$ . . . .	1.70   ,,
Total. . . . .	5.33   ,,
Found . . . .	5.14   ,,

By taking the essential constituents of each patina, *i.e.*, the stannic hydroxide and basic carbonates, and calculating them on 100, the composition of the pure patina without admixture with foreign impurities is obtained, thus :—

	Patina A.		Patina B.	Patina of patchwork.
$\text{CuCO}_3, 2\text{CuO}_2\text{H}_2$ . .	85.83	$\text{CuCO}_3, 3\text{CuO}_2\text{H}_2$ . .	95.11	56.08
$2\text{PbCO}_3, \text{PbO}_2\text{H}_2$ . .	13.01	$2\text{PbCO}_3, \text{PbO}_2\text{H}_2$ . .	4.49	24.62
$\text{SnO}_3\text{H}_2$ . . . . .	1.16	$\text{SnO}_3\text{H}_2$ . . . . .	0.40	19.30
				D. B.

**Process for Bleaching Ozokerite.** By C. O. CHEMIN (*Dingl. polyt. J.*, 253, 413—415). The object of this process is to prevent the darkening of ozokerite during bleaching. The author proposes to melt the material in water kept at a temperature of  $70^\circ$ . After allowing the impurities to settle, the melted matter is decanted into a retort, treated with 5—15 per cent. flowers of sulphur, and distilled by the aid of superheated steam. The distillation, which is not fractional, gives a yellow crystalline product. The action of the sulphur is partly mechanical and partly chemical. The product of the distillation may be treated in either of two ways (1) by subjecting cakes of the distillate to pressure, the plates of the press being at a temperature of  $35^\circ$  to  $50^\circ$ , thus expressing the oils and hydrocarbons melting at low temperatures; (2) by reducing the distillate to powder, and subjecting it to a spray of water at a temperature of  $45^\circ$  to  $60^\circ$ , so as to wash away the oils and readily fusible hydrocarbons. Instead of water, amyl alcohol or other solvent of hydrocarbon oils may be employed at

the ordinary temperature. The product obtained according to either of these modes of treatment is melted on a water-bath at 35–70°, and 20 per cent. amyl alcohol added. It is then mixed intimately, and cast into moulds. The resulting cakes after being subjected to pressure are melted, digested for four hours in agitation with bone-black, and filtered through animal charcoal. On cooling, the product, amounting to 79–80 per cent. of the crude material treated, is white, hard, and sonorous. The residue resulting from the last treatment is distilled so as to recover the solvents employed. It is then mixed with the crude material to be subsequently treated. From 25 to 40 per cent. of residue from treatment of petroleum or naphtha may be mixed with the ozokerite, which is said to facilitate the working of this process. D. B.

**Dari as a Source of Alcohol.** By J. HOLZAPFEL (*Bied. Centr.*, 1884, 569–570).—Dari is the commercial name of the seeds of *Sorghum nigrum*, *caffrorum*, and *saccharatum*, containing on an average 64 to 72 per cent. of starch. The author recommends the use of this seed in brewing and distilling. Steamed under a pressure gradually increasing to 3 atmospheres, it yields a clear brown fluid mash. Used in the proportion of 2351 grams to 52 kilos. malt, the results are high in spirit of good flavour, tasting better than maize spirit; at the present prices of dari and maize, there is also an economy in its use. J. F.

**Degeneration of Yeast.** By J. C. JACOBSEN (*Bied. Centr.*, 1884, 638–640).—Brewers' yeast deteriorates and grows wild if no change is made; the beer made loses quality and assumes an unpleasant taste. To prevent this, fresh yeast must be introduced from elsewhere, or else cultivated by the manufacturers. E. W. P.

**Loss of Sugar in Beetroots when Stored.** By WIETERSHEIM and others (*Bied. Centr.*, 1884, 565–566).—When sugar-beets are stored they lose, between October and January, up to 1½ per cent. in polarisation, which it is calculated amounts to an annual loss of 24 millions of marks on the beetroot production of Germany. It is found that the loss is greater in proportion as the outside temperature is high, and much more so when the temperature of the interior of the heap is high. A common mode of storing is in large pits, in which the roots are heaped up and covered with earth; it is advised that they should not be stored underground, but on the ground, and lightly covered with peat fibre, damp being almost as injurious as warmth. The loss of sugar is also influenced by the quality of the beet, its mode of culture, manuring, and other causes. J. F.

**Preparation of Sugar from Molasses.** By E. v. LIPPMANN and others (*Bied. Centr.*, 1884, 635–638).—The composition of lime saccharate precipitated by alcohol is  $C_{12}H_{22}O_{11}, CaO + 2H_2O$ , the crystalline water being lost at 100°. If lime be added to the solution of the saccharate, the anhydrous dicalcium salt is precipitated; and if the precipitation occurs at a high temperature, 2–3 mols.  $H_2O$  are found in combination. The tricalcium salt with  $3H_2O$  is produced if

well dried finely powdered lime is stirred up for a long time with the saccharate; this compound is soluble in 200 parts of cold water. The tricalcium salt loses 2 mols.  $\text{CaO}$  when mixed with sugar solution, part of the lime being then precipitated; the sugar crystals obtained by precipitation of the lime by carbonic anhydride are somewhat different in form from the normal crystals, being proportionally somewhat longer, although the angles remain the same. Harperath's patent consists in the employment of dolomite in place of strontium, &c.; when the burnt mineral is introduced into the sugar solution, monocalcium and magnesium saccharates are first formed, also some soluble "bisaccharate," the impurities are thus carried down by the lime and magnesia, and a further addition of the ignited dolomite results in the formation of insoluble tricalcium and magnesium saccharates; the tricalcium and magnesium saccharate is absolutely insoluble in water, thus a gain over the calcium salt is obtained, which latter salt is the source of loss in sugar to the extent of  $\frac{1}{2}$  per cent. Moreover a high temperature is unnecessary, neither does the compound spontaneously decompose so readily as the pure calcium saccharate; the composition is said to be  $x\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{CaO})_3(\text{H}_2\text{O})_2 + y\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{MgO})_2\text{H}_2\text{O}_2$ . Boivin's and Loiseau's patent for the separation of grape-sugar consists of the following processes: 700 grams of slaked lime is mixed with 1 kilo. molasses which has previously been diluted to 12–15° Baumé; this mixture is cooled, saturated with carbonic anhydride, and the resulting mass is then pressed through a perforated cylinder into threads 3–5 mm. thick; afterwards the impurities are removed by stirring up with lime-water, and the washed calcium compound is then decomposed by carbonic anhydride, the carbonate removed, and the sugar solution evaporated. Scholvien publishes a patent to modify the osmotic process; by this method the molasses is to be heated to 100°, and the sugar precipitated as the tricalcium compound; the filtrate, heated to 60°, is then submitted to osmosis.

E. W. P.

**Purification of Molasses.** By J. GANS (*Bied. Centr.*, 1884, 645).—Gans has patented a process in which he employs aluminium hydroxide and dialyses at 60°; to prevent the gelatinous separation of the alumina, a small quantity (0.001 per cent.) of tartaric acid is added.

E. W. P.

**Extracting Sugar from Molasses.** (*Dingl. polyt. J.*, 253, 421–426 and 519–529.)—In extracting the sugar from molasses and syrups, according to Scheibler's strontia process, the formation of strontium bisaccharate may be prevented by introducing fresh quantities of molasses and strontium hydroxide into the mother-liquor resulting from the filtration of the monosaccharate originally produced. This treatment is repeated several times until the consistency of the mother-liquor renders the process impracticable in consequence of the accumulation of non-saccharine matter. After repeating this operation 6 or 8 times, the residue contained only 3 per cent. of the sugar present in the molasses when attacked.

Dureas gives a description of the ammonium chloride osmose process, as worked at the Haussy sugar refinery in France. The syrup obtained from product I is treated with about 1 per cent. ammonium

chloride, and heated to boiling. It is then run into collecting tanks, heated to 100°, and purified by osmose with 10 to 12 parts of water at 70—75°. The resulting syrup is added to fresh juice.

According to Stutzer, the recovery of sugar from molasses by the precipitation process depends on the separation of calcium saccharate from an alcoholic solution of molasses. It has been ascertained by experiment that the precipitation of the sugar is best effected in an alcoholic solution of molasses by previously slaking the lime with alcohol. The separation of calcium saccharate by the addition of ground lime to an alcoholic solution of molasses is not only slow but also uncertain, a circumstance which proves that calcium hydroxide combines more readily with sugar than the oxide, especially in alkaline saccharine solution (molasses). Barium and strontium hydroxides behave in a similar manner.

Referring to Steffen's defecation process, the following methods have been patented by the Brunswick Engineering Works:—On mixing an aqueous solution of sugar with a compound of calcium saccharate containing more lime than the quantity required to form monosaccharate, in such proportions that the total amount of sugar present in the mixture contains more than 15 parts calcium oxide to 100 parts sugar in the solution, it is possible to separate the sugar by treating the solution with lime at a temperature not exceeding 25°, the resulting compound of calcium saccharate being sparingly soluble in water at that temperature. On adding to a solution of calcium saccharate, at a temperature not exceeding 35°, a compound of calcium saccharate of a higher degree of saturation than the quantity of lime necessary to form the monobasic salt, almost the whole of the sugar contained in the mixture is separated in the form of a calcium saccharate compound, insoluble in water at a temperature below 35°.

Bärthlein has worked the defecation process at the Sarstedt Sugar Refinery with molasses of different composition, and obtained satisfactory results even with Indian molasses. He found that a solution containing 7 per cent. sugar gave the best yield.

Frost has recovered the sugar from 300 tons molasses according to the defecation process. This quantity was worked up in four weeks with a yield of 52—52.5 per cent. of filling substance.

Scholvien recommends the purification of calcium saccharate solution by osmosis. For this purpose the hot solution of molasses is treated with lime so that 1 mol. sugar equals 3 mols. lime. The mixture is then filtered, and the filtrate purified by osmosis at 60° and added to fresh juice.

Hüttgen uses two osmose apparatus. He places one apparatus 35 cm. above the other. The liquor from the former passes through a heating apparatus interposed between both apparatus, and is brought to a temperature of 97° before it is purified by passing through the second osmose apparatus. It is said that a saving in fuel is effected, as only half the usual quantity of wash-water has to be evaporated.

D. B.

**Formation of Grape-sugar from Starch.** By H. ENDEMANN (*Bied. Centr.*, 1884, 568—569).—Endemann employs phosphoric in-

stead of sulphuric acid in the process of inversion. 1000 kilos. air-dried starch, 2000 kilos. water, and 50 kilos. of phosphoric acid are heated in a closed vessel at  $140^{\circ}$ ; the addition of a small quantity of nitric acid assists the reaction. The acid is removed by addition of a base forming insoluble combinations, preferably lime; the presence of gypsum in the glucose is thereby avoided. J. F.

**Preparation of Concentrated Acetic Acid.** By T. GÖRING (*Dingl. polyt. J.*, 254, 90—91).—The author proposes to treat solutions of acetic acid with ethyl ether, ethyl acetate, amyl alcohol, or other similar liquid, insoluble or only slightly soluble in water; salts may or may not be added at the same time. By systematic treatment, the whole of the acetic acid is concentrated in the liquid so added. The extract may be treated with a suitable base, as lime, by which acetate is formed, and the extracting medium is ready for application afresh. If concentrated acetic acid be required, an ether of low boiling point is employed, which is separated from the extracted acid by distillation. For very concentrated acid, the extract is first treated with some substance capable of removing the small quantity of water taken up, such as magnesium or calcium chloride, &c. If pure acid is required, the extract is subjected to an inverse process, the acid is washed out with water in a second apparatus, whilst the extracting medium retains certain impurities taken up along with the acetic acid. J. T.

**C. Thiel's Pasteurising Apparatus for Milk.** By W. FLEISCHMANN (*Bied. Centr.*, 1884, 632—633).—Thiel's apparatus consists of a hollow double-walled cylinder, the division between the two walls being filled with water at  $74-80^{\circ}$ ; the inner division is covered by a perforated lid which admits of the milk flowing in streams down the outside of the inner and heated wall; from there the milk passes to a Laurence's refrigerator. Milk may thus be heated from  $6^{\circ}$  to  $25-60^{\circ}$  to the amount of 750 kilos. per hour. E. W. P.

**Bitter Milk.** By LIEBSCHER (*Bied. Centr.*, 1884, 561—562).—In a well-managed farm in Thuringia, the butter which had hitherto found a ready sale became repulsively bitter, and consequently unsaleable; this led to strict examination, and it was eventually found that a number of the cows in the earliest portion of their milking yielded a bitter milk, and that when this was taken in a separate vessel the remainder was sweet.

It was therefore suspected that the stalls had in some manner become infected with bacteria, which had commenced their progress into the udders of the cows without having made much advance. Both stalls and cattle were thoroughly disinfected. Carbolic acid was sprinkled about frequently, and the cow's udders washed twice daily with lukewarm water and then with dilute carbolic acid; in three days the bitterness had disappeared, and the milk and butter tasted sweet. J. F.

**Quality of Butter made by different Processes.** By M. SCHRODT (*Bied. Centr.*, 1884, 562—565).—It has been said that butter

made by the centrifugal process is deficient in keeping properties, and not of so good quality as hand-made butter; the author therefore collected numerous samples of both descriptions from different localities, and submitted them to the judgment of experts who classified them into seven classes; the results are tabulated, and show that all processes when carefully conducted give equally good butters, and that the centrifugal method can produce butters which are quite as good as hand made, both in respect of their quality and keeping properties. J. F.

**Preparation of Quinaldine.** (*Dingl. polyt. J.*, **254**, 91—92.)—According to the *Actiengesellschaft für Anilinfabrikation* of Berlin, if 3 mols. of aldehyde be allowed to act on an aqueous or alcoholic solution of 2 mols. aniline hydrochloride at the ordinary temperature, there is produced not the salt of the liquid quinaldine,  $C_{10}H_9N$ , but the salt of a new fixed base,  $C_{18}H_{20}N_2$ . The mixture must be kept cool with ice, and the reaction requires two or three days for its completion. By evaporation, the hydrochloride of the new base is obtained as a brownish-red mass easily soluble in water. Alkalis precipitate the base from a solution of the salt, in white flakes which, when dried, form a white amorphous powder insoluble in water, only slightly soluble in boiling alcohol, but easily in hot benzene or amyl alcohol. On heating the hydrochloride of this base alone or in presence of metallic chlorides, *e.g.*, ferric chloride, quinaldine hydrochloride is produced. By fusing it with zinc chloride, the double chloride of zinc and quinaldine is produced. Instead of ordinary aldehyde, corresponding quantities of paraldehyde, aldol, or acetal can be employed, and other aniline salts in place of aniline hydrochloride. By the action of aldehyde, &c., on the salts of other primary aromatic bases, such as orthotoluidine or naphthylamine, compounds are obtained analogous to the base  $C_{18}H_{20}N_2$ , and similarly convertible into quinaldine. J. T.

**Dyeing with Alizarin Colours on Indigo-blue Cloth.** (*Dingl. polyt. J.*, **253**, 474.)—According to Delory of Rouen, calico dyed with indigo is mordanted with aluminium acetate or sodium aluminate, and dyed with alizarin in the presence of Turkey-red oil. A small amount of alizarin suffices to produce the desired effect of imparting to the blue a slight purple cast, and adding considerably to the strength of the colour and its power to withstand the action of alkalis. The mordant used for darker blues is iron acetate or a mixture of the latter with aluminium acetate. The alizarin employed is always of the purest blue shade. D. B.

**History of Alizarin-blue.** By A. SCHEURER (*Dingl. polyt. J.*, **253**, 297—299).—In September, 1875, Schaeffer drew the attention of the *Comité de Chemie* to an observation made by Strobel, that on exposing goods dyed red with alizarin to the fumes of nitrous anhydride an orange colour was obtained, which is not attacked by soap solution. Rosenstiehl recognised this new chemical compound as mononitroalizarin, and its manufacture on a large scale was soon



commenced. Two years later he was engaged in the formation of a new dye, viz., alizarin-blue.

On the 27th June, 1877, Prudhomme, in a communication laid before the *Société Industrielle de Mulhouse*, described the simultaneous discovery of two colouring-matters, a blue and a brown dye, obtained by heating mononitroalizarin (alizarin-orange) with glycerol and sulphuric acid. These colours were prepared on a large scale within a few months of their discovery.

Brunk, of the *Badischen Anilin Fabrik*, recognised the brown dye as amidoalizarin, formed as a bye-product of the reaction. He isolated the blue colouring matter and studied its properties. In December, 1877, the Baden Aniline Works brought this colour into commerce in the form of a 10 per cent. paste. Its insolubility in water and acetic acid, however, prevented it from being used extensively.

Dollfus proposed to dye alizarin-blue on cloth mordanted with nickel, the result being the production of permanent and bright shades. Köchlin and Prudhomme recommended to fix the blue on cotton with chromium acetate. The colour was found to resist the action of chlorine and similar substances, but assumed a grey tinge on exposure to the light. Brunk then made a further improvement by bringing the blue into the market in a soluble form. For this purpose alizarin-blue is treated with hydrogen sodium sulphite. The resulting compound is soluble in water, and is fixed with chromium acetate, a pure blue colour being obtained, which is said to resist the influence of light even better than indigo.

Graebe assigned to alizarin-blue the formula  $C_{17}H_9NO_4$ , and it must therefore be regarded as the quinoline of alizarin. The blue marked S, sold by the *Badischen Fabrik*, contains 2 mols. hydrogen sodium sulphite to 1 mol. alizarin-blue, thus:  $C_{17}H_9NO_4, 2NaHSO_3$ .

D. B.

**Preparation of Persulphocyanogen by Electrolysis.** By F. GOPPELSROEDER (*Dingl. polyt. J.*, 254, 83).—On passing a galvanic current through an aqueous solution of potassium thiocyanate, a yellow amorphous body appears at the positive electrode, which behaves exactly like persulphocyanogen. In the cold there is scarcely any reaction, but on heating the conversion is rapidly effected, and the orange-yellow flocculent precipitate merely requires to be collected and washed with cold water. The liquid at the positive electrode is strongly acid, and at the negative one strongly alkaline. Much gas is evolved at the negative electrode, the nature of which has not yet been investigated. The author will also further investigate the yellow product, which so far appears to be the dye mentioned by Schützenberger in his work *Traité de Chimie général*, ii, 620. Schützenberger gives the probable formula as  $C_3N_3HS_3$ . The author has also produced the dye and fixed it on vegetable and animal fibres by the same process. The author cites Prochoroff's method of producing the yellow dye *kanarin*, and ascribes the application of it to calico-printing to H. Schmidt. In an appendix, the author acknowledges that A. Lidow formed the same compound from ammonium thiocyanate by electrolysis.

J. T.

**Preparation of a Dye-stuff from Cotton-seed Oil.** By J. LONGMORE (*Dingl. polyt. J.*, **253**, 535).—The author proposes to melt the precipitate thrown down in the refining of cotton-seed oil, and saponify it with pulverised caustic soda or a solution of soda. The solution which contains the colouring matter of cotton-seed oil is allowed to settle, and the resulting soap dissolved in water and salted out with caustic soda or soda-ley. This treatment is repeated several times until the soap has attained a sufficient degree of purity.

D. B.

**Manufacture of Santonin in Turkestan.** By C. O. CECHE (*Dingl. polyt. J.*, **253**, 474—476).—The author mentions that in Tschemkeut, a town in the province of Syr-Daria, in Turkestan, a large factory is in course of erection, for the purpose of extracting santonin from worm-seed (*Artemisia satonica* and *maritima*). This plant is cultivated in some parts of South America, and in the valley of the River Arissi, in the Tschemkeut district. It contains from 1·8 to 2·3 per cent. of santonin, and is called "Darmena" by the natives. About 1600 tons of seeds are collected annually by the Kirghiz-Kazaks during the month of August, and sent on caravans into the interior of Russia, whence the product is forwarded to Moscow. In medicine, worm-seed is either employed *per se*, or is treated by chemical means, to extract the santonin therefrom, which is used as a remedy for ascarides. Santonin is considered a valuable preparation, 1 kilo. being sold at from 40 to 60 shillings.

D. B.

**"Red Spots" in Light Rose Dye.** By E. LAUBER (*Dingl. polyt. J.*, **254**, 41—42).—The author finds that these "red spots" cannot be prevented, however finely the alizarin may be powdered, neither are they prevented if the thickening paste is stirred into the alizarin paste, as recommended by the Badischen Aniline und Soda firm. He finds the cause of this defect to be the employment of an unnecessary excess of mordant. The measured amount of mordant should be first mixed with a small amount of thickening, to this the rest of the thickening is then added by degrees, and finally the alizarin.

J. T.

**Bleaching Indigo-blue and Turkey-red by Electrochemical Means.** By F. GOPPELSROEDER (*Dingl. polyt. J.*, **253**, 430).—Scheurer has recently laid before the *Comité de Chimie* of the *Société Industrielle de Mulhouse*, an interesting communication on the bleaching of indigo and Turkey-red by the aid of gaseous chlorine. He showed that on printing a thickened solution of caustic alkali on certain parts of indigo-blue or Turkey-red cloth, the printed places could be bleached with chlorine gas very readily. The author therefore made a series of trials, the object being to ascertain whether this process could be applied to the bleaching of indigo or Turkey-red by electrolysis. He found that on saturating indigo-blue or Turkey-red cloth with a solution of potassium nitrate or sodium chloride, previously treated with caustic alkali, and placing the cloth between platinum plates, forming the two electrodes, it was possible to destroy both colours.

D. B.

## General and Physical Chemistry.

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**Refractive Indices of Crystallised Alums.** By C. SORET (*Compt. rend.*, 99, 867—869).—By means of the instrument previously described (*Compt. rend.*, 95), the author has determined the refractive indices of many alums for the lines *a*, B, C, D, E, *b*, F, G, of the solar spectrum. He has also determined the specific gravities of the alums by means of the hydrostatic balance. In the following table, only the refractive indices for D and the specific gravities are given :—

	$n_D$ .	Sp. gr.
Ammonium aluminium alum . . . .	1·45939	1·631
Sodium " " . . . .	1·43884	1·667
Methylamine " " . . . .	1·45410	1·568
Potassium " " . . . .	1·45645	1·735
Rubidium " " . . . .	1·45660	1·852
Cæsium " " . . . .	1·45856	1·911
Thallium " " . . . .	1·49748	2·257
Ammonium indium " . . . .	1·46636	2·011
" gallium " . . . .	1·46552	1·745
Potassium " " . . . .	1·46499	—
Ammonium chromium " . . . .	1·48418	1·719
Potassium " " . . . .	1·48137	1·817
Rubidium " " . . . .	1·48151	1·946
Thallium " " . . . .	1·52280	2·236
Ammonium iron " . . . .	1·48482	1·713
Potassium " " . . . .	1·48169	1·806
Rubidium " " . . . .	1·48234	1·916
Cæsium " " . . . .	1·48378	2·061
Thallium " " . . . .	1·52365	2·385

The molecular volume is not constant for the different terms of the same series, but it seems to vary in a definite manner for the corresponding terms of the aluminium, chromium, and iron series.

In passing from one alum to another, the variation in the refractive index is sensibly the same in the three series, thus following a law which has been observed in other series of compounds. It is worthy of note, however, that the refractive index of sodium alum is much less than that of potassium alum, whilst in the case of the chlorides the sodium salt is intermediate between the potassium and ammonium compounds.

The author's value for the refractive index of thallium alum is much higher than that obtained by Fock.

Methylamine alum is intermediate between the sodium and potassium compounds, and it would seem as if, in the aluminium series, the refractive index varied continuously with the molecular weight of the alkaline radicle.

C. H. B.

**Inversion of the Electromotive Force of a Copper Iron Junction at a High Temperature.** By F. F. LE ROUX (*Compt. rend.*, **99**, 842—844).—A bar of iron was bent in the form of a horse-shoe, and attached at each end to a copper bar. This couple was placed in a furnace and heated nearly to the melting point of copper, a current of about 350 ampères being passed through the couple. Any change in the temperature of the junction was detected by observing a change in the relative luminosity of the junction, the results of ocular observation being confirmed by the action of the radiation on a gelatino-bromide plate.

It was found that at about 1000° a current passing from the copper to the iron raises the temperature of the junction, whilst at the ordinary temperature a current in the same direction cools the junction.

C. H. B.

**Electrolysis of Silver Fluoride, Chlorate, and Perchlorate.** By G. GORE (*Chem. News*, **50**, 150).—A moderately strong solution of silver fluoride acidified with hydrochloric acid is a very good conductor of electricity, and is very readily decomposed by means of silver electrodes and a current from a cell containing zinc and platinum in dilute sulphuric acid. Crystals of silver are rapidly deposited at the cathode, whilst the anode soon becomes rough, grey in colour, and very friable. In special experiments, no evidence could be obtained to show that this loss of cohesion was due to the diffusion of liberated fluorine through the silver.

When a solution of silver chlorate is electrolysed by sheet silver electrodes and a current from two Smee's cells charged with very dilute sulphuric acid (1 vol. of acid to 50 of water), conduction is good, and silver is freely deposited only at first; the deposit being loose, and not very white. The anode also is soon coated with a black film, presumably silver peroxide, which seems to stop the current; it is permanently blackened, although but slowly corroded. With one Smee's cell, the deposit is formed slowly, and is more coherent. This solution requires a feeble current, a large cathode, and a much larger anode.

When silver perchlorate is similarly electrolysed, conduction is very good, and loose, bulky, silky crystals of silver are soon deposited at the cathode, whilst the anode quickly becomes black, the current at the same time becoming much diminished. With one cell and a more dilute solution, conduction is free, the deposit is smaller, and the anode becomes less dark. A silver wire anode soon becomes corroded and loosely coated with a black substance; this falls off and is ultimately replaced by a thick green coating; no gas is evolved. The solution requires a large cathode and a rather small anode.

D. A. L.

**Electro-deposition of Carbon and Silicon.** By G. GORE (*Chem. News*, **50**, 113—114).—Carbon, silicon, and boron have each been deposited during the electrolysis of certain fused mixtures.

*Carbon is deposited* when a current from 10 Smee's elements is passed through a fused mixture of 200 grains of sodium hydroxide, 170 grains precipitated silica, and 610 grains of mixed anhydrous sodium and potassium carbonates, the anode being sheet platinum,

the cathode a wire of the same metal; the deposition of carbon is, however, probably due to a secondary reaction of this character: silicon is first deposited and this reacts with the alkaline carbonates, and causes the separation of carbon. The same phenomenon occurs when a mixture of 475.2 grains of 97.1 per cent. sodium carbonate and 217.4 grains sodium borofluoride is similarly treated, and apparently also in the electrolysis of aqueous or alcoholic oxalic acid. The deposited carbon is not crystalline.

*Carbon is not deposited* either during the electrolysis of sodium and potassium carbonates, using eight Smee's cells and platinum electrodes at a red heat, or when boric acid is included in the mixture, or by the electrolysis of any of the following: potassium cyanide, oxalic acid in solution in hydrochloric or nitric acid, sodium formate or formic acid, carbonic oxide and anhydride, pyrogallol, liquid hydrocyanic acid saturated with carbonic oxide, fuming sulphuric or syrupy phosphoric acids saturated with dry carbonic anhydride; or from dilute sulphuric acid over which coal-gas was passing during the 14 days the electrolysis was continued. Carbon tetrachloride does not yield carbon under the influence of an electric current. These experiments were conducted under different conditions as to strength of current, length of time, temperature, and composition of electrodes.

*Silicon is deposited* when a fused mixture of 300 grains of 97.1 per cent. potassium carbonate and 442 grains of potassium silicofluoride is electrolysed, as described above in the carbon-deposition experiments.

D. A. L.

**Relation between the Ordinary Thermometer and the Weight Thermometer.** By E. BARBIER (*Compt. rend.*, 99, 752—753).—A demonstration of the theorem that if the ordinary thermometer and the weight thermometer agree at the two fixed points, they agree at all temperatures.

C. H. B.

**Attraction of Homogeneous Molecules.** By C. SCHALL (*Ber.*, 17, 2555—2577).—In order to interpret experiments on the relation between the rates of evaporation of liquids and their molecular weights and heats of expansion, the author has more particularly studied the phenomena of cohesion and adhesion of liquids, a subject of interest to the chemist as dealing with the attraction of homogeneous and heterogeneous molecules. The method of investigation was based on that of the so-called adhesion plates, which consists, in outline, in suspending a plate of glass from one pan of a balance, and counterpoising it; the plate being adjusted to a level, a dish containing the liquid to be examined is placed under it, and then raised until the surfaces of the liquid and glass are in contact. To the opposite pan of the balance, weights are added until the glass is severed from the liquid; this excess of weight is then noted. The apparatus used, together with devices for levelling the plate and for the complete severance of the liquid and glass, are described in detail in the paper. As the attractive force between two contingent molecules within a liquid is proportional to their mass and inversely proportional to the square of the distance between them, and as increase of distance is correlative with decrease of specific gravity and also with that of cohesion,

it follows that a decrease of the latter caused by warming the liquid is proportional to the square of the former. But the superficial expansion, which is equal to the  $\frac{2}{3}$  power of the cubical, is inversely proportional to the specific gravity. As the superficial expansion increases, the number as also the mass of molecules under the plate and their correlative cohesion diminishes, and therefore the latter diminishes in direct proportion to the  $\frac{2}{3}$  power of the specific gravity. Hence if  $s$  and  $s_1$  be the specific gravities for any two degrees of temperature,  $G$  and  $G'$  the excess of weight necessary for the disruption of the plate, then

$$G = G' \left( \frac{s}{s_1} \right)^2 \left( \frac{s}{s_1} \right)^{\frac{2}{3}}.$$

Experimental results are tabulated which demonstrate the validity of the formula, and of the law deduced therefrom, that the force by which homogeneous molecules are attracted varies in direct proportion to the square of the specific gravity, and also to the mass of the molecules. From the experimental results can be deduced the diminution of cohesion for each degree of temperature, and thus the critical point at which the cohesion is *nil*.

But the results obtained with some of the liquids examined, especially water, benzene, and its derivatives, are not in strict accordance with the law enunciated above, so that it would appear that the force of cohesion is dependent to some extent on the chemical constitution of the liquid. In the case of two liquids, it is further demonstrated that the relation between the respective cohesions and also their specific gravities at boiling points within restricted limits of pressure are approximately identical.

These experiments are also of importance in regard to the phenomenon of capillary attraction, a force which depends on the difference between the force of cohesion of the molecules of the liquid with one another, and of adhesion to the molecules of the glass. If the force of attraction as represented by the capillary height =  $h$ , that of the adhesion of the liquid to the glass =  $a$ , and of the cohesion of the liquid =  $c$ , then—

$$h = a - c.$$

The form of the meniscus is concave if  $a > c$ , but convex if  $a < c$ . But from the above formula,  $\frac{a}{a'} = \left( \frac{s}{s'} \right)^2 \left( \frac{s}{s'} \right)^{\frac{2}{3}}$ , then if the capillary heights are  $h$  and  $h'$  at two different temperatures, then  $h = a - c$ , and  $h' = a' - c'$ , it follows that  $h' = \frac{a - c}{\left( \frac{s}{s'} \right)^2 \left( \frac{s}{s'} \right)^{\frac{2}{3}}}$ , or  $h' = \frac{h}{\left( \frac{s}{s'} \right)^2 \left( \frac{s}{s'} \right)^{\frac{2}{3}}}$ .

Experimental results are also adduced in support of these formulæ, although water and liquid sulphur offer instances of marked exception; it is thus probable that the molecular constitution of these liquids is the cause of the discrepancy.

V. H. V.

**Relation between Molecular Weight and Velocity of Evaporation of Liquids.** By C. SCHALL (*Ber.*, 17, 2199—2212).—This

paper contains a description of the apparatus and method of working employed by the author in his experiments with benzene, carbon bisulphide, and water (Abstr., 1884, 551).

Experiments with substances of nearly coincident molecular weight and boiling point :—

	Calculated.	Found.
{ Phenol .....	$m = 94$	95·57, 95·11, 95·11
{ Aniline .....	$m = 93$	91·48, 91·91, 91·91
{ Toluene .....	$m = 92$	93·85
{ Valeraldehyde .....	$m = 86$	84·3
{ Monochlorobenzene .....	$m = 112·5$	108·2
{ Acetic anhydride .....	$m = 102$	106
{ Benzoic chloride .....	$m = 140·5$	144·3, 144·5
{ Ethyl benzoate .....	$m = 150$	145·7, 145·2

Experiments with substances of nearly equal molecular weights, but of different boiling points :—

	Calculated.	Found.
{ Ethyl acetate .....	$m = 88$	86·32, 87·76
{ Amyl alcohol(fermentation) .....	$m = 88$	89·71, 87·76
{ Benzaldehyde .....	$m = 106$	104·7, 110
{ Acetic anhydride .....	$m = 102$	103·3, 98·27

Experiments with substances of unequal molecular weights, but of nearly coincident boiling points :—

	Calculated.	Found.
{ Acetic chloride .....	$m = 78·5$	78·06
{ Acetone .....	$m = 58$	58·33
{ Alcohol .....	$m = 46$	41·2, 41·2
{ Benzene .....	$m = 78$	87·12, 87·12
{ Toluene .....	$m = 92$	94·28
{ Phosphorus oxychloride ..	$m = 153·5$	149·8

Substances with different boiling points and different molecular weights :—

	Calculated.	Found.
{ Benzene .....	$m = 78$	75·5, 75·5
{ Toluene .....	$m = 92$	95·04, 95·04
{ Methyl alcohol .....	$m = 32$	30·66
{ Propyl alcohol .....	$m = 60$	62·63
{ Ethyl alcohol .....	$m = 46$	45·48
{ Isobutyl alcohol .....	$m = 74$	74·84
{ Isobutyl alcohol .....	$m = 74$	65·65
{ Amyl alcohol(fermentation) ..	$m = 88$	99·19

Recent determinations of heats of vaporisation show that these are proportional to the time of vaporisation. In the following table,  $t$  is the boiling point at which the heat of vaporisation  $L$  was determined,  $DL$  the product of the latter multiplied by the theoretical density,  $m$  the calculated, and  $m'$  the found molecular weight :—

	<i>t.</i>	L.	DL.	<i>m.</i>	<i>m'.</i>
Water.....	100°	532·0 cal.	331·7	—	—
Wood spirit .....	66·5°	261·7 "	290·1	32	36·6
Ethyl alcohol.....	7·8	206·4 "	328·8	46	46·4
Amyl alcohol .....	131	120·0 "	368·7	88	89·0
Ethyl acetate .....	74	105·0 "	320·0	88	91·2
Methyl butyrate....	93	86·0 "	343·8	102	111·2
Oil of lemon .....	165	69·5 "	327·4	136	138·3
Oil of turpentine...	156	68·5 "	322·7	136	139·8
Butyric acid .....	164	114·0 "	347·5	88	84·0
Ethyl valerate .....	113·5	68·4 "	308·0	130	140·0

The author has further compared the velocity of evaporation of acetic acid with that of toluene, amyl alcohol, and isobutyl alcohol, and the results obtained show that the molecular weight of acetic acid at its boiling point is 89·8. This may also be calculated from Favre and Silbermann's determinations of its heat of vaporisation, and likewise for formic acid, the molecular weight 69.

A. K. M.

**On Crystallisation. Observations and Conclusions.** By G. BRÜGELMANN (*Ber.*, 17, 2359—2372).

**Stability of Compounds.** By W. ALEXÉEFF (*Jour. Russ. Chem. Soc.*, 16, 641—642).—The author communicates his researches as to the conditions determining the stability of a compound in the presence of an excess of one or the other of its constituents. The results agree with what he found with regard to the stability of hydrates of alcohols in their aqueous and alcoholic solutions. The difference in the stability of hydrates determines the difference of the vapour-tensions, at one and the same temperature, for two solutions, which are formed by water, and a liquid capable of yielding a hydrate. Moreover, in an aqueous solution, this tension is always smaller when the formula of the hydrate is  $A + nH_2O$ ,  $n$  being generally greater than unity. With solutions formed by water and ether, a difference in temperature of 8° corresponds with equal tensions.

B. B.

**Phenomena of Condensation.** By D. MENDELÉEFF (*Jour. Russ. Chem. Soc.*, 16, 643—644).—The author remarks that the phenomena of condensation, as shown in the case of the formation of solutions or on diluting some liquids, is analogous to what takes place when spherical bodies of different diameters, such as samples of different seeds (pease and millet), are mixed together. When spherical bodies are mixed, as may be shown by experiment or by geometrical analysis, the weight of a measure containing a large number of such small spheres of both kinds is greater than the mean calculated from the weight of both kinds taken alone. In the same manner, the sp. gr. of a solution is greater than it should be, when calculated from the sp. gr. and the quantity of the constituent liquids. The analogy in the change of volumes which takes place in both the above cases shows that when a



small bulk of light spheres of small diameter is added to heavier spheres of large diameter, the sp. gr. of a cubic measure of the last may become greater, exactly as the first addition of water to normal sulphuric acid raises its sp. gr. The above geometric question is, unfortunately, up to the present inaccessible for full geometric analysis, and the experimental investigation is rendered very difficult by the impossibility of obtaining the necessary balls of regular size and equal diameters.

Experiments with mixtures of millet and gunpowder, however, have convinced the author that the above phenomenon exists, but it is only a statical representation of a dynamical phenomenon which takes place in the case of dissolution as a simple act of chemical association of heterogeneous particles.

B. B.

### Connection between Pseudo-solution and True Solution.

By W. W. J. NICOL (*Chem. News*, 50, 124).—Arguing from the molecular theory of solution, according to which the dissolution of a salt in water is the result of the attraction of the water molecules for a single salt molecule exceeding that of the attraction of the salt molecules for one another, the author demonstrates that the difference between pseudo-solution and true solution lies only in the degree of subdivision of the solid. For by this theory dissolution depends greatly upon cohesion, and where cohesion is small dissolution is easy, and *vice versa*; taking barium sulphate as an example, the cohesion is great, the solubility almost *nil*; if, however, the cohesion is diminished by any means, then the finely-divided salt will remain suspended in water for a long time, that is, in a state of pseudo-solution, which shows that the water molecules alone were not able to overcome the cohesion, but this being to a certain extent overcome, *pseudo-solution* is the result. Supposing now the insoluble salt could be resolved into its molecules, that is, further subdivided, then it is easy to conceive that it would be possible to dissolve it to a great extent in water, and produce a *true solution*, from which the solid would separate but slowly, owing to the solid molecules seldom coming in contact in sufficient numbers for their mutual attraction to overcome that of the water for them. As examples of such cases, the author refers to the fact that many almost insoluble compounds are precipitated with extreme slowness from cold dilute solutions.

D. A. L.

**Rise of Solutions in Capillary Tubes.** By M. GOLDSTEIN and A. DAMSKI (*Jour. Russ. Chem. Soc.*, 16, 642—643).—According to Valson, the rise of a large number of solutions of salts in capillary tubes is inversely proportional to their specific gravities. This erroneous conclusion is explained by the fact that Valson worked with solutions showing no great differences in sp. gr. and, therefore, in the rise. Very different results are obtained on using solutions of great concentration (2 or 3 gram-mols. of salt to 1 litre of water) and narrower tubes; here the specific gravities and rise in the tubes differ conspicuously from those of pure water, and the regularity, shown by Valson, does not exist, *e.g.* :—

	Height of rise. <i>h</i> .	Sp. gr. <i>d</i> .	<i>h.d.</i>
Pure water . . . . .	118.2	1.000	118.2
KCl $\frac{1}{4}$ mol. wt. to 1 litre	117.4	1.009	118.4
" $\frac{1}{3}$ " " ..	117.3	1.016	119.1
" $\frac{1}{2}$ " " ..	116.4	1.025	119.3
" 1 " " ..	115.3	1.048	120.8
" 2 " " ..	114.1	1.100	125.5
" 3 " " ..	112.4	1.155	129.8

The value *h.d* equals that for water only for very dilute solutions.

The determinations of the above values for potassium chloride, bromide, and iodide have shown that the rise of solutions of potassium bromide of different degrees of concentration is the mean of the rise of corresponding solutions of potassium iodide and chloride, the molecular weight of KBr being the mean between those of KCl and KI:—

Solutions.	Height of rise.		KBr.	
	KCl.	KI.	calc. from	
	<i>a</i> .	<i>b</i> .	$\frac{a+b}{2} = c.$	found
$\frac{1}{4}$ mol. in 1 litre..	117.4	—	—	115.9
$\frac{1}{3}$ " ..	117.3	114.5	115.5	115.2
$\frac{1}{2}$ " ..	116.4	113.0	114.7	114.6
1 " ..	115.3	108.5	111.9	111.3
2 " ..	114.1	100.2	107.1	107.1
3 " ..	112.4	93.5	102.9	102.8

B. B.

**Capillary Phenomena in Relation to Constitution and Molecular Weight.** By J. TRAUBE (*Ber.*, 17, 2294—2316).—All the experiments described in this paper were made with *aqueous* solutions of organic substances: the advantages of the use of such solutions over organic liquid compounds, being the much greater height at which the former stand in capillary tubes, and the much greater differences in capillary height shown in the case of closely related substances. Voluminous tables are given, at once showing the difference in capillary height caused by difference in the concentration of solutions of the same substance, and comparing the capillary heights of unlike substances in solutions of the same degree of concentration. The following are amongst the more important conclusions drawn from these experiments:—1. The capillary height of the solution of an organic body decreases with increasing concentration. Equal differences of height are not, however, caused by equal increments of concentration, the rate of difference first attaining a maximum, and then diminishing. 2. In a homologous series, the capillary height diminishes with increasing molecular weight. The difference reaches its maximum sooner in more concentrated than in more dilute solutions. 3. Isomeric substances, although of related constitutions, have not necessarily equal capillary heights. With regard to the capillary relations of different organic series, the author gives

the following as the result of his observations:—An increase in capillary height is observed in passing, 1, from the fatty alcohols to the corresponding aldehydes or acids; 2, from the fatty acids to the hydroxy-acids; 3, from the monohydric to the di- and tri-hydric alcohols; 4, from the normal and iso-alcohols to the tertiary alcohols; 5, from the ethereal salts of formic acid to isomeric ethereal salts of the higher fatty acids; 6, from compounds of the propyl series to those of the allyl series. Probably an increase in capillary height also occurs in passing from aldehydes to isomeric ketones, and from fatty acids to their monosubstituted halogen-derivatives, although on further substitution a decrease occurs; further observations are required on these two points. Aldehydes show a lower capillary height than the corresponding fatty acids in concentrated solutions, but in dilute solutions the reverse is observed. Normal alcohols show a lower capillary height than iso-alcohols in concentrated solutions.

A. J. G.

**Mutual Relations of the Physical Properties of the Elements.** By H. FRITZ (*Ber.*, 17, 2160—2165).—This paper contains a table of most of the heavy metals, with their melting points, specific gravities, atomic weights, and specific heats; from these, it may be shown by calculation that the product of the atomic heat by the relative heat is equal to the cube root of the product of the melting point multiplied by the specific heat,  $As \cdot Ds = \sqrt[3]{ts}$ ; A being the atomic weight,  $s$  the specific heat,  $D$  the sp. gr., and  $t$  the melting point. The elements are arranged in groups in which different values are substituted for  $t$ . In the case of lithium, sodium, and potassium, the value  $\frac{t + 50}{2.50}$  is substituted for  $t$ ; in the case of magnesium and aluminium the value  $\frac{t + 50}{7.4}$ , and in that of strontium and barium  $\frac{t + 50}{30}$ .

If the metals be arranged I, according to the amount of heat liberated by their union with oxygen and chlorine, and II, according to their conductivity for heat, the one series will be found to be the reverse of the other.

A. K. M.

### A General Statement of the Laws of Chemical Equilibrium.

By H. LE CHATELIER (*Compt. rend.*, 99, 786—789).—The author extends and modifies Van t'Hoff's general statement of the chemical equilibrium of a system by including in it the "condensation" of the system, that is, pressure, concentration, number of molecules in unit volume, &c., and by giving it a form similar to that of the laws relating to changes of equilibrium which effect mechanical work. Reversible chemical changes are thus brought into the class of reciprocal phenomena.

When a system in stable chemical equilibrium is acted on by an external cause which tends to alter the temperature or condensation either of the whole system or of some of its parts, the system can only

undergo such internal modifications as would, if they had taken place spontaneously, have produced a change of temperature or condensation of the contrary sign to that resulting from the action of the external cause.

These modifications are generally progressive and incomplete. They are, however, sudden and complete if they can take place without changing the individual condensation of the different homogeneous parts of the system, whilst at the same time they alter the condensation of the system as a whole.

They are *nil* when their occurrence cannot produce changes analogous to those due to the external cause.

Although modifications may be possible, they do not necessarily take place. In cases where no change occurs and the system remains unaltered, the original stable equilibrium becomes unstable, and the system can then only undergo such modifications as tend to bring it back to stable equilibrium. Many well-known reactions, including the phenomena of fusion, evaporation, solution, &c., are cited as examples.

C. H. B.

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### Inorganic Chemistry.

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**Combustible Organic Matter in the Air.** By A. MUNTZ and E. AUBIN (*Compt. rend.*, **99**, 871—874).—The amount of combustible organic matter in the air was determined by two methods. In the first, a known volume of air, carefully filtered from suspended matter and purified from carbonic anhydride, was passed over heated cupric oxide, and the volume of carbonic anhydride produced by the combustion of the organic matter was measured. In the second, the amount of carbonic anhydride in 1000—1500 litres of air was determined by the method previously described (*i.e.*, by passing the air through a tube containing potash pumice), and an equal volume of air taken at the same place and at the same time was passed over heated cupric oxide, and the amount of carbonic anhydride formed was estimated. The difference between this amount and that already existing in the air is the amount produced by the combustion of the organic matter. Both methods gave identical results.

At Paris, the amount of carbonic anhydride formed by the combustion of the atmospheric organic matter varies between 3 and 10 vols. per 1,000,000 vols. of air. At Vincennes the volume varies from 2.0 to 4.7 per million, the mean result for October, November, and December, 1882, being 3.3 vols. It would seem, therefore, that the amount of organic matter in the air is represented by a volume of carbonic anhydride equal to one-hundredth part of the volume of carbonic anhydride existing as such in the atmosphere.

If it is assumed that all the combustible carbon is present in the air as methane, the volume of the hydrogen contained in the latter will be 16 per million of air, or, in Paris, 33 vols. per million, a number which agrees well with the lower values found by Boussingault.

When electric discharges are passed through the air, the combustible organic matter is more or less completely burnt, and there is little doubt that the electric discharges which take place in the lower regions of the atmosphere destroy a considerable proportion of the combustible organic matter which the latter contains. C. H. B.

**Reactions with Carbon and some of its Compounds.** By G. GORE (*Chem. News*, 50, 124—126).—When white or red phosphorus, or powdered arsenic or antimony or sodium, are added to fused potassium cyanide; or when aluminium or sodium phosphide, or a mixture of sodium phosphide with zinc, is added to fused potassium and sodium carbonates; or when sodium carbonate is decomposed at a low red heat by phosphorus vapour; or when a mixture of red phosphorus and ammonium carbonate is dropped into a red-hot porcelain crucible, a black substance separates, which in some cases is found to be carbon. Carbon is also obtained when coal-gas is passed over red-hot finely-powdered ferric oxide, or over just fused argentic fluoride or chloride, or over chloride of lead or copper. Arsenic and antimony do not visibly decompose fused sodium and potassium carbonates; neither is carbon set free when ammonium carbonate is added to fused sodium; nor when coal-gas is passed over fused cadmium chloride or silver iodide; nor in several experiments wherein numerous hydrocarbons, in various solvents, were exposed to metals and metallic couples. Several unsuccessful attempts at deoxidising carbonic anhydride are also described along with many experiments wherein many substances alone and in contact were immersed in various solutions of metallic salts containing carbon in combination, and in these solutions when exposed to carboniferous vapours, but in all cases without any deposition of carbon. The chlorides of carbon proved equally useless as sources of carbon, even resisting the influence of potassium, which however formed an alkaline salt with carbon tetrachloride; potassium or sodium, dissolved in anhydrous liquid ammonia at 60° F., behaved in a similar manner with carbon bromide and sulphide, and with anhydrous sodium carbonate or formate, or ammonium oxalate. On passing dry ammonia gas into liquid carbon dichloride containing potassium, gas was evolved, and a red powder formed; with naphtha instead of the chloride, the potassium only became red. Carbon is insoluble in anhydrous liquid cyanogen, sulphuric chloride, phosphorus trichloride, antimony pentachloride, anhydrous liquid hydrofluoric and hydrochloric acids: chlorides of carbon and bisulphide of carbon were also found to be insoluble in the last two acids, but they are soluble in liquid cyanogen. Many experiments with carbon bisulphide are described; for example, when silver and platinum in contact are immersed in it, after some time the silver blackens; in the same way lead and mercury yield a black powder soluble in nitric acid. Thallium also blackens, but no action could be observed with tin, or magnesium and platinum, or with boron fluoride; tin tetrachloride, thallium chloride, and cyanogen are dissolved by it, and it precipitates mercuric chloride from its solution in ether. The solutions of sulphur and phosphorus in carbon bisulphide give no reaction when exposed in an atmosphere of carbonic anhydride; zinc remains bright

in the sulphur solution and potassium and platinum in contact cause no free carbon to separate from it; aluminium and magnesium become dull, but are not corroded by prolonged exposure in the phosphorus solution. When a solution of silver nitrate with a piece of platinum partly immersed in it was exposed to carbon bisulphide vapour continuously for seven weeks, all the silver was precipitated; magnesium, aluminium, or silver partly immersed in water exposed to the same vapour, were unaltered; when, however, the silver was in contact with platinum, the liquid became dark and the silver above it blackened. A liquid which dissolved selenium was obtained by passing the vapour of selenium over charcoal powder kept at a full red heat.

D. A. L.

**Polymorphism of Silicon Phosphate.** By P. HAUTEFEUILLE and J. MARGOTTET (*Compt. rend.*, 99, 789—792).—Hydrated silica dissolves readily when heated with orthophosphoric acid, and the solution deposits crystallised silicon phosphate in forms varying with the temperature at which the deposition takes place. When an intimate mixture of phosphoric acid and hydrated silica is gradually heated to 260°, about 5 per cent. of silica is dissolved, and a still larger proportion can be obtained in solution by gradually heating a mixture of phosphoric acid with silicon chloride.

When the solution of silica in phosphoric acid is allowed to cool below 260°, it deposits crystals having the appearance of flattened discs. Similar crystals are obtained when the solution is mixed with strong sulphuric acid and heated for some time at a temperature somewhat above the boiling point of the latter. These crystals are hexagonal prisms, frequently macled in the same manner as lamellar hæmatite. They act strongly on polarised light, and are somewhat rapidly attacked by water, but do not alter in contact with alcohol.

If the temperature of the solution of silica is gradually raised from 260° to about 360°, it deposits an abundance of very thin hexagonal lamellæ, which act feebly on polarised light and resemble tridymite in appearance. They are, however, distinguished from the latter by the fact that they yield silver phosphate when fused with silver nitrate. These lamellæ are not altered by alcohol, but are slowly attacked by water with formation of phosphoric acid and soluble silica.

If the solution of silica is heated rapidly, it remains limpid up to about 700°, but between 700° and 800° it deposits regular octahedra which are almost always modified by cubical faces. This form of silicon phosphate has already been described (*Abstr.*, 1883, 782).

When phosphoric acid containing only a small proportion of silica is rapidly heated to about 900—1000°, the crystals obtained are monoclinic prisms which act strongly on polarised light. At a high temperature, these prisms are more stable than the other forms. If phosphoric acid saturated with silica is slowly heated to 1000°, a mixture of all four forms is obtained; but if the temperature is maintained the lamellæ and octahedra are quickly attacked, whilst the prisms continue to increase.

The crystals were analysed by fusion with silver nitrate. They all have the composition  $P_2O_5, SiO_2$ . The hexagonal crystals are formed

below  $300^{\circ}$ , the lamellæ resembling tridymite at about  $360^{\circ}$ , the regular octahedra between  $700^{\circ}$  and  $800^{\circ}$ , and the monoclinic prisms between  $800^{\circ}$  and  $1000^{\circ}$ . This polymorphism is not due to different groupings of the same crystalline elements, for the hexagonal crystals are attacked by water, which has no action on the octahedra or prisms.

Other phosphates behave in a similar manner.

C. H. B.

**Crystalline Phosphorous Anhydride.** By J. M. CABELL (*Chem. News*, 50, 209).—The mixture of oxides obtained by burning phosphorus with a limited supply of air was placed at both ends of a long tube, the intervening space being empty; carefully dried and purified hydrogen was then passed through the tube and the foremost portion of the oxides gently heated. At about  $350^{\circ}$  F. crystals were deposited in the empty portion of the tube, whilst the residue became semi-fused. The crystals, apparently monoclinic, could not be measured; when quickly transferred to litmus-paper they did not redden it for some seconds. Their solution did not give phosphoric acid reactions with either ammonium molybdate or magnesia mixture; but after warming with nitric acid both reactions were obtained. It is hence inferred that these are crystals of *phosphorous anhydride*.

D. A. L.

**Arsenic Trifluoride.** By H. MOISSAN (*Compt. rend.*, 99, 874—876).—Arsenic trifluoride was obtained by heating calcium fluoride and arsenious oxide with sulphuric acid. It forms a colourless, very mobile liquid, which boils at  $63^{\circ}$  under a pressure of 752 mm., and fumes in the air; sp. gr. = 2.734. It dissolves a certain quantity of iodine, acquiring a purple-red colour, and combines with bromine at a gentle heat, forming a crystalline compound. When heated to dull redness in a glass vessel, it yields silicon fluoride and arsenious oxide, but no metallic arsenic is liberated:  $4\text{AsF}_3 + 3\text{SiO}_2 = 2\text{As}_2\text{O}_3 + 3\text{SiF}_4$ . When the arsenious fluoride is electrolysed in a platinum vessel by means of 25 Bunsen elements arranged in series, metallic arsenic is deposited, and a gas is given off at the positive electrode which, although made of platinum, is superficially attacked.

C. H. B.

**Specific Gravity of Sulphuric Acid.** By D. MENDELÉEFF (*Ber.*, 17, 2536—2541).—A reply to Lunge (Abstr., 1884, 1256), in which the author upholds the correctness of his density 1.8371 at  $\frac{15^{\circ}}{4^{\circ}}$  as against that of 1.8384 found by Lunge.

L. T. T.

**Octosulphates.** By R. WEBER (*Ber.*, 17, 2497—2503).—By heating carefully dried sulphates with excess of sulphuric anhydride, the author has obtained a series of well characterised salts of the general formula  $\text{M}'_2\text{O}_8\text{SO}_3$ . The product while still hot consists of two layers, the upper one being unchanged anhydride. The salt solidifies as it cools, and the still liquid anhydride may be poured off, and the last traces carefully distilled off at about  $60^{\circ}$ .



The *potassium salt*,  $K_2O, 8SO_3$ , melts in the presence of excess of sulphuric anhydride at  $80^\circ$ : when isolated, it is slowly decomposed at the boiling point of the anhydride, yielding first  $K_2O, 2SO_3$ , and finally  $K_2SO_4$ . It crystallises from the fused mass in prisms. *Rubidium* and *cæsium* behave exactly like potassium, but no corresponding sodium or lithium compound could be obtained. The *ammonium salt*,  $(NH_4)_2O, 8SO_3$ , is formed even more easily than the potassium salt. Of the heavy metals, *thallium* alone seems capable of forming an octosulphate. Its crystals seem to be isomorphous with those of the potassium compound, and, like the latter, it yields a disulphate,  $Tl_2O, 2SO_3$ , when heated. *Silver* yields a *disulphate*,  $Ag_2O, 2SO_3$ , under this treatment, but no higher sulphate could be obtained. The analogy of thallium to potassium, and the dissimilarity therefrom of sodium and lithium, are noticeable.

L. T. T.

**Action of Water on Double Salts.** By F. M. RAOULT (*Compt. rend.*, 99, 914—916).—The author has determined the molecular reduction of the freezing point produced by various double salts containing more than one molecule of the acid radicle, with the results given in the following table, where A is the observed molecular reduction and S the sum of the molecular reductions produced separately by each of the simple salts of which the double salt is composed:—

	A.	S.		A.	S.
$K_2SO_4, MgSO_4 \dots$	57.7	58.2	$2KCl, MgCl_2 \dots$	117.2	116.0
$K_2SO_4, ZnSO_4 \dots$	58.1	57.2	$2KCl, CuCl_2 \dots$	116.8	115.6
$K_2SO_4, FeSO_4 \dots$	56.5	58.0	$2AmCl, HgCl_2 \dots$	68.4	90.1
$K_2SO_4, CuSO_4 \dots$	58.3	57.0	$2NaCl, PtCl_4 \dots$	54.2	96.3
$K_2SO_4, Al_2(SO_4)_3 \dots$	82.4	83.4	$2KI, HgI_2 \dots$	50.8	90.0?
$K_2SO_4, Fe_2(SO_4)_3 \dots$	85.0	82.1	$2KCy, HgCy_2 \dots$	57.3	81.9
$K_2SO_4, Cr_2(SO_4)_3 \dots$	83.2	84.4	$KCy, AgCy \dots$	31.1	66.0?

It is evident that many double salts, especially the alums and the double sulphates and double chlorides of the magnesium group of metals, produce a molecular reduction of the freezing point practically identical with the sum of the molecular reductions produced separately by each constituent salt. In other words, they behave in solution as if the constituent salts were merely mixed and not in actual combination, a result which agrees perfectly with thermochemical observations. In the case of the last five salts in the table, however, this does not hold good, and it follows that these double salts are not completely decomposed by water, a result agreeing with thermochemical observations, which show that the formation of each of the last three is accompanied by the development of a considerable amount of heat.

From these results, it follows that a comparison of the observed molecular reduction of the freezing point produced by a given double salt with the sum of the partial reductions produced by each constituent, will show whether the double salt is or is not completely decomposed when it is dissolved in water.

If it is assumed that the molecular reduction produced by a given

double salt is equal to the mean molecular reduction of the potassium salts containing the same number of atoms in the molecule (a supposition which is supported by the known behaviour of silver potassium cyanide), it is possible to calculate the amount of decomposition which each salt experiences when dissolved. Some of the numbers thus obtained are given in the following table. They represent that fraction of the molecule of the double salt which is decomposed by water:—

KCy + AgCy + water (2 litres) .....	0·00
2KCy + HgCy <sub>2</sub> + water (10 litres).....	0·38
2KI + HgI <sub>2</sub> + water (4 litres) .....	0·38
2AmCl + HgCl <sub>2</sub> + water (10 litres).....	0·59
2NaCl + PtCl <sub>4</sub> + water (4 litres) .....	0·26
2KCl + MgCl <sub>2</sub> and analogous chlorides ....	1·00
K <sub>2</sub> SO <sub>4</sub> + MgSO <sub>4</sub> „ sulphates ....	1·00
K <sub>2</sub> SO <sub>4</sub> + Al <sub>2</sub> SO <sub>4</sub> „ „ ....	1·00

C. H. B.

**Magnesium Suboxide.** By G. GORE (*Chem. News*, **50**, 157).—Beetz (*Phil. Mag.*, 1866, 269) observed, when magnesium electrodes were used for the electrolysis of a solution of sodium chloride, that a black substance was formed on the positive pole, and from the fact that it evolved hydrogen in contact with certain aqueous solutions, he concluded that it was magnesium suboxide.

The author has observed a similar phenomenon under the following conditions:—

When magnesium alone is partly immersed in water and exposed to coal-gas, carbonic anhydride, vapour of CCl<sub>4</sub> or C<sub>2</sub>Cl<sub>4</sub>, or when it is immersed in a mixture of absolute alcohol with glacial acetic acid; the deposition is slight with magnesium in liquefied glacial acetic acid alone, or in a solution of toluene or formic acid in absolute alcohol, or in a mixture of glacial acetic, with either sulphuric acid or vegetable naphtha. On the other hand, the deposition is more rapid in all these cases when the magnesium is in contact with either platinum, gold, silver, or iron, and most rapid with palladium. Magnesium and platinum in contact produce it when they are immersed in a solution of either creosote, toluene, or xylene in vegetable naphtha, or in a solution containing 1·25 mm. of hydrochloric acid per ounce of water. The black deposit is also formed when magnesium alone is immersed in solutions of the following salts containing 5 grains of salt per ounce of water:—potassium, sodium, ammonium, lithium, barium, strontium, calcium, and magnesium chlorides, bromides of the first three, and potassium iodide, the sodium chloride solution giving the largest amount. In all cases it appeared within the first few days, subsequently disappearing with the simultaneous formation of white magnesium hydroxide. From all these facts, it is evident that the black substance comes from the magnesium. It turns white when heated to a temperature below redness. It is soluble in dilute nitric acid, yielding a green solution owing to reduction; hydrochloric and sulphuric acids dissolve it with effervescence. Its hydrochloric acid solution contains magnesium chloride only. These results confirm

Beetz's conclusion, namely, that this substance is *magnesium sub-oxide*.  
D. A. L.

**Copper Peroxide.** By G. KRÜSS (*Ber.*, **17**, 2593—2597).—The experiments by Thénard seemed to indicate the formation of a copper peroxide by the agitation of cupric oxide with a dilute solution of hydrogen peroxide. In this paper, a description is given of a repetition of this work, and it is shown that if very finely divided cupric oxide is agitated for several days with hydrogen peroxide there is gradually formed an olive-green precipitate of composition  $\text{CuO}_2 \cdot \text{H}_2\text{O}$ . It is decomposed at a temperature of  $6^\circ$  when moist, but is far more stable when dry. The formation of this compound points to the tetratomicity of copper. From other experiments, it would appear that an oxide can be obtained intermediate in composition between cupric oxide and peroxide, formed by heating cupric oxide with caustic potash, or potassium or sodium chlorides.  
V. H. V.

**Decomposition of Cupric Oxide by Heat.** By E. J. MAUMENÉ (*Compt. rend.*, **99**, 757—759).—A criticism on the papers by Debray and Joannis (this vol., pp. 21 and 22).  
C. H. B.

**Action of Hydrogen Sulphide on Metallic Silver.** By J. M. CABELL (*Chem. News*, **50**, 208—209).—The author has made four experiments in which very carefully cleaned pure silver was exposed under certain varying conditions to a current of pure hydrogen sulphide, which was first carefully dried. The results tend to show that, in absence of water, hydrogen sulphide does not act on silver at the ordinary temperature.  
D. A. L.

**Silver Hydroxide.** By J. D. BEUCE (*Chem. News*, **50**, 208).—When dilute solutions of silver nitrate and potassium hydroxide, in 90 per cent. alcohol, are mixed at the ordinary temperature, in quantities containing equivalent amounts of the two substances ( $\text{AgNO}_3$  and  $\text{KHO}$ ), the usual granular brown precipitate of silver oxide is formed. When, however, the mixing is effected at very low temperatures, the precipitate which forms is flocculent, and has less and less colour as the temperature is lowered, until at about  $-50^\circ \text{F}$ . the precipitate is almost white. This white precipitate soon becomes coloured, and at  $-40^\circ \text{F}$ . is already pale brown. The white precipitate is presumably *silver hydroxide*, and is but slightly soluble in water.  
D. A. L.

**Hydrated Aluminium Sulphate.** By P. M. DELACHARLONNY (*Compt. rend.*, **99**, 800—801).—When a moist mass of crystals of normal aluminium sulphate,  $\text{Al}_2\text{SO}_4 \cdot 16\text{H}_2\text{O}$ , is cooled to  $6-8^\circ$ , crystals of a new hydrate,  $\text{Al}_2\text{SO}_4 \cdot 27\text{H}_2\text{O}$ , are gradually formed. These crystals are hexagonal prisms modified by faces of the rhombohedron in the same manner as crystals of diopase. They are formed only below  $9.5^\circ$ , and when exposed to the air at ordinary temperatures they give off water and are reconverted into the hydrate  $\text{Al}_2\text{SO}_4 \cdot 16\text{H}_2\text{O}$ . The same change is brought about by mechanical disturbance, such as crushing the crystals with a pestle. The crystals can, however, be preserved in

closed flasks without undergoing any alteration. The formation of this hydrate from the ordinary hydrate is much facilitated by mixing the latter with some ready-formed crystals of the former. C. H. B.

**Reaction between Ferric Oxide and certain Sulphates at High Temperatures.** By SCHEURER-KESTNER (*Compt. rend.*, 99, 876—877).—When a mixture of two parts of calcium sulphate and one part ferric oxide is heated to bright redness, it fuses, the whole of the sulphur is expelled, and a residue of ferric and calcium oxides is left, soluble in dilute acids. Even acetic acid gradually removes the calcium in the cold. During the decomposition, sulphuric anhydride is first evolved, and afterwards, as the temperature rises, sulphurous anhydride and oxygen. Probably the mixture fuses and calcium oxide and ferric sulphate are formed, the latter being afterwards decomposed. By adding a flux, such as calcium chloride or fluoride, decomposition takes place at a lower temperature, but the crucible is much corroded.

Lead sulphate is decomposed in the same way at a somewhat lower temperature. The residue dissolves in dilute nitric acid without evolution of nitrogen oxides, and acetic acid gradually dissolves out the lead in the cold. Magnesium sulphate behaves in a similar manner, but does not fuse, and only sulphurous anhydride and oxygen are given off without any sulphuric anhydride. C. H. B.

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## Mineralogical Chemistry.

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**The Brown Coal of Istria and Dalmatia.** By LODIN (*Dingl. polyt. J.*, 253, 534).—The author gives an account of the strata of Istria and Dalmatia belonging to the eocene period, and of the geology of the deposits of brown coal. The coal in the Carpano Valley has the following composition:—I, from the lower beds; II, from the lower beds altered by exposure to atmospheric influences; III and IV, from the upper beds; and V, an average sample.

	I.	II.	III.	IV.	V.
Water .....	1·46	1·70	1·57	1·53	1·56
Carbon .....	63·69	59·58	64·26	65·86	63·35
Hydrogen .....	5·03	4·60	4·85	4·84	4·83
Oxygen .....	13·12	12·36	13·03	11·45	12·49
Nitrogen .....	1·79	1·18	1·04	1·22	1·31
Sulphur .....	7·53	7·33	8·53	8·93	8·08
Ash .....	8·84	14·96	8·29	7·68	9·94
Total .....	101·46	101·71	101·57	101·01	101·56
Yield of coke .....	55·07	58·10	52·88	58·07	56·03

D. B.

**Analysis of Cassiterite from King Co., N. Carolina.** By J. D. BRUCE (*Chem. News*, **50**, 209).—The sample examined is of light brown colour, transparent, and of resinous lustre. Its sp. gr. is 6.956. For analysis, the powdered mineral was gently heated in a glass tube in a current of hydrogen, the residue digested with hydrochloric acid, the tin precipitated as stannous sulphide, and the filtrate treated in the usual manner. The following are the results of analysis :—

SnO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Loss on ignition.	Insoluble residue.	Total.
95.176	1.455	0.277	0.020	0.218	2.841	99.987

The insoluble residue is probably chiefly silica.

D. A. L.

**Apatite from Amelia Co., Virginia.** By G. H. ROWAN (*Chem. News*, **50**, 208).—This specimen of apatite occurs imbedded in felspar in a vein of coarse granite, from which large sheets of mica and many rare minerals are obtained. The crystals are white and translucent, with a shade of violet, and are cracked in various directions, laminated parallel to face *i* ii, of vitreous lustre, and quite fragile. When heated, it phosphoresces with a yellow light. Its sp. gr is 3.161. The analytical data give the following :—

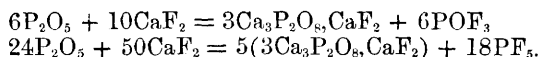
CaO.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	F.	Cl.	Loss on ignition.	Insoluble residue.	Total (less 1.39 O for F)
53.94	0.19	0.81	41.06	3.30	trace	0.81	0.63	99.33

This corresponds with the formula  $\text{Ca}_3\text{P}_2\text{O}_8 + \frac{1}{3}\text{CaF}_2$ . The insoluble residue is probably due to adhering mica.

D. A. L.

**Fluor-apatites.** By A. DITTE (*Compt. rend.*, **99**, 792—794).—A metallic phosphate, *e.g.*, calcium phosphate, is heated to redness for five or six hours in a platinum crucible with three times its weight of normal potassium fluoride and a large proportion of potassium chloride. The product is allowed to cool and the residue treated with water, when crystals of fluor-apatite,  $3\text{Ca}_3\text{P}_2\text{O}_8, \text{CaF}_2$ , remain undissolved. These crystals are quite free from chlorine, a result which agrees with Guntz's observation, that the heat of formation of calcium fluoride is higher than that of the chloride. The amount of potassium fluoride present should not be more than 5 per cent. of the amount of potassium chloride, for if the alkaline fluoride is in excess the calcium phosphate is converted into fluoride. According to Guntz, the heats of formation of barium and strontium fluorides at the ordinary temperature are somewhat lower than the heats of formation of the corresponding chlorides. It would appear, however, that at high temperatures this is not the case, for if barium or strontium phosphate is substituted for calcium phosphate in the foregoing reaction, the corresponding fluor-apatite is obtained perfectly free from chlorine.

Another method of preparation is as follows:—Calcium fluoride and phosphoric anhydride in suitable proportions are heated for several hours with a large proportion of potassium chloride, and the product is extracted with water after cooling. In this case the reaction can be represented by one of the following equations :—



The alkaline chloride simply plays the part of a solvent, from which the apatite crystallises. The phosphoric anhydride may be replaced by ammonium phosphate, care being taken to avoid excess of the latter. The corresponding barium, strontium, and magnesium compounds are obtained in a similar way.

Calcium fluor-phosphate obtained in this way sometimes forms long prisms, the faces of which are striated parallel with the lateral edges, sometimes short prisms terminated by hexagonal pyramids. They are not altered by heat, but dissolve slowly in dilute acids in the cold, more rapidly when heated. The barium, strontium, and magnesium compounds have the same form and properties. Iron fluor-phosphate forms transparent green needles which are difficult to separate from the fused amorphous matter which accompanies them.

C. H. B.

**Origin and Formation of Masses of Calcium Phosphate in Sedimentary Rocks. Their Relation to the Iron Ores and Clays of the Siderolithic Horizon.** By DIEULAFAIT (*Compt. rend.*, 99, 813—816).—This paper is mainly a *résumé* of conclusions already published (*Abstr.*, 1884, 1272) respecting the origin of the phosphorites found in limestone caverns.

Comparative examinations of many specimens of iron ores and clays from the siderolithic horizon, and of the limestones with which they are in contact, leads to the conclusion that the origin of the former is intimately connected with the latter, and that the iron ores and clays have been formed by the destruction of the calcareous rocks, and are really the residues left when the limestones were dissolved by percolating water from lakes and lagoons. The iron ores derive their phosphorus from the original limestones, and are more highly charged with phosphorus the higher the proportion in which this element existed in the limestones and the percolating water.

C. H. B.

**Phosphatic Deposits of the South-east of France.** By P. DE GASPARIN (*Compt. rend.*, 99, 839—841).—The large proportion of phosphoric acid in the fossils of the gault in the south-east of France has in all probability been derived from water containing phosphoric acid or phosphates in solution. This water has percolated through the sandy matter composing the grits in which the fossils are enclosed, and the phosphoric acid has been retained by the calcium previously existing in the shells in the form of carbonate. This supposition is supported by the fact that in many localities in the south-east of France there are large phosphatic, chalky, and ferruginous masses of rock, the formation of which can readily be explained in the same way.

The solution of phosphoric acid or phosphates may possibly have been derived from volcanic rocks by the action of the acid water also evolved during volcanic disturbances.

C. H. B.

**Investigation of a Saltpetre-earth from Turkestan.** By N. LJUBAVIN (*Jour. Russ. Chem. Soc.*, **16**, 617—638).—A sample of this earth was sent to the author from Fort Nukus, Province Amu-Dari. Colonel Albanof found that the natives of the oasis Amu-Daria prepare nitre by boiling this earth with water and evaporating the solution until it crystallises on cooling; they use it for the manufacture of gunpowder without any further purification. They regard this impure nitre as a poison. This earth covers an area of 7 square kilos. on the frontier of China, over the ruins of the old city of Kunia-Ugrentch, in a country with very little rain.

The earth, which is of a pale cinnamon colour, is dry, and can be readily pulverised between the fingers. It has a feebly alkaline reaction.

The author gives a detailed account of the method used for the quantitative determination of the different constituents of the earth; he finds that when calcium oxalate is precipitated from a solution containing alkalis, appreciable quantities of the latter are carried down with the oxalate.

In the following table, the results of the analysis are given in percentages of the earth, dried at 100°, 96·21 parts of which are equal to 100 parts of air-dried earth:—

*Portion Soluble in Water.*

$N_2O_5$ .	Cl.	$SO_3$ .	$K_2O$ .	$Na_2O$ .*	$SiO_2, Fe_2O_3, Al_2O_3$ .
6·28	7·82	2·35	2·57	8·32	0·02
	CaO.	MgO.	Soluble humus.		
	1·34	0·80	0·15 =		29·65
Subtracted oxygen equivalent to 7·82 of Cl					1·76
					27·89

\* Containing  $Li_2O$ .

*Portion Soluble in Hydrochloric Acid.*

$SO_3$ .	$SiO_2$ .	$P_2O_5$ .	$K_2O$ .*	$Fe_2O_3$ .	$Al_2O_3$ .	$CaO$ .†	MgO.	$Mn_2O_4$ .
0·38	0·018	0·314	0·58	2·91	2·75	7·58	2·50	0·11 = 17·142

\* Containing  $Na_2O$  and  $Li_2O$ .

† Containing  $SrO$ .

*Portion Insoluble in Water and Hydrochloric Acid.*

Organic substances and water.	$SiO_2$ .	$Al_2O_3$ .*	CaO.	MgO.	$K_2O$ .	$Na_2O$ .
1·84	37·39	5·60	0·51	0·25	1·46	1·37 = 48·42

\* Containing traces of  $Fe_2O_3$  and  $P_2O_5$ .

Total nitrogen .....	1·75
Organic nitrogen in this .....	0·13



Substances soluble in water.....	27·89
” ” hydrochloric acid....	17·14
Carbonic anhydride .....	5·73
Substances insoluble in water and in acids .	48·42
	— —
Total .....	99·18

To this sum should be added the quantity of water of crystallisation contained in the salts at 100°.

The constituents of the portion of earth soluble in water may be grouped as follows:—

Potassium nitrate.....	5·52	} all nitrates, 10·61.
Sodium nitrate.....	4·05	
Magnesium nitrate . ....	1·04	
Sodium chloride .....	12·90	
Calcium sulphate .....	3·25	
Magnesium sulphate .....	0·66	

The total of calcium sulphate, including the portion soluble in hydrochloric acid, is 3·93 per cent., and from this  $\text{CaSO}_4 + \text{H}_2\text{O} = 4·97$ . This gypsum, according to Puchard, plays an important part in the formation of nitre under the influence of a ferment.

The analysed earth may be regarded as comparatively very rich in nitre, for in other countries earths containing only 0·26 per cent. are worked up with success.

On comparing the composition of the portion of earth insoluble in water, A, with the analysis of mud suspended in the water of Amu-Dari (Schmidt and Dorandt), B, the author finds a striking similarity between the two:—

	A.	B.
$\text{SO}_3$ .....	0·53	0·00
$\text{SiO}_2$ .....	52·47	49·62
$\text{P}_2\text{O}_5$ .....	0·46	0·22
$\text{CO}_2$ .....	8·04	8·17
$\text{K}_2\text{O}$ .....	2·87	2·15
$\text{Na}_2\text{O}$ .....	1·92	1·65
$\text{Fe}_2\text{O}_3$ .....	4·19	4·73
$\text{Al}_2\text{O}_3$ .....	11·57	17·43
$\text{CaO}$ .....	11·35	11·16
$\text{MgO}$ .....	3·86	2·61
$\text{Mn}_3\text{O}_4$ .....	0·15	0·15
Humus ....	0·96	} 2·11
Water.....	1·63	
	100·00	100·00

B. B.

**Blue Quartz from Nelson Co., Virginia.** By R. ROBERTSON (*Chem. News*, 50, 297).—This quartz is found associated with felspar in varying quantities; it has a characteristic waxy lustre, varies in colour from pale to deep blue, and is penetrated by numerous thin

brown films. A thin section under the microscope shows a network of thin, acicular, brown crystals throughout the mass, so that, when magnified 400 times, it presents an appearance similar to that of sagenite when seen by the naked eye. Some of the crystals are twinned, forming geniculations common with rutile. The section is yellow by transmitted, and blue by reflected light.

A fragment fused before the hot-blast blowpipe retains its blue colour. Analysis yields the appended results per cent. :— $\text{Fe}_2\text{O}_3$ , 0.539;  $\text{TiO}_2$ , 0.069;  $\text{SiO}_2$  (by difference), 99.392. Rutile is frequently found in the granulitic rocks of the district, and the magnetic iron ores of the locality contain large amounts of titanium oxide. D. A. L.

**Analysis of Pinite from Madison Co., N. Carolina.** By C. L. REESE (*Chem. News*, 50, 209).—This mineral is found in amorphous irregular masses. It is white, with a tinge of green, has a waxy lustre, a rough fracture, and is greasy to the touch. Its hardness is nearly 3; its sp. gr. = 2.822. The average of two analyses by the author gave the results under A, whilst under B are the results obtained from the analysis of this mineral made by C. H. Slaytor in Bunsen's laboratory at Heidelberg.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	Water.	Total.
A. . . .	47.28	36.47	0.28	trace	11.40	0.74	4.39	= 100.56
B. . . .	47.31	38.11	—	—	13.37	—	1.05	= 99.84

D. A. L.

**Amazon Stone from Amelia Co., Virginia.** By C. C. PAGE (*Chem. News*, 50, 208).—This variety of amazon stone, in moderate sized crystals, is of uniform light green, or bluish-green colour; whilst in large crystals the colour shades off to white. Its cleavage lustre is vitreous, or pearly; its sp. gr. = 2.564. A thin section seen under the microscope shows the characteristic grated structure of microcline, along with a slight admixture of plagioclase. Analysis yields the following figures:—

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	Total.
64.12	16.84	2.28	0.32	0.26	13.34	1.88	= 99.04

D. A. L.

**Albite from Amelia Co., Virginia.** By R. ROBERTSON (*Chem. News*, 50, 208).—This variety of albite is occasionally found within masses of albite. It is bluish-grey, and slightly opalescent. Cleavage on O pearly, and regularly striated on i i pearly. Its sp. gr. is 2.618. Analysis gave :—

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$
67.06	21.72	1.59	0.03	10.01	0.39

corresponding approximately with 6 mols. albite and 1 mol. anorthite.

D. A. L.

**Analysis of Chrysocolla from Gila Co., Arizona.** By R. ROBERTSON (*Chem. News*, 50, 209—210).—The mineral consists of coal-black particles united by a much smaller quantity of bright

bluish-green chrysocolla. The dark portion is purple-black, opaque, with sub-metallic to dull lustre, fracture rough, with tendency to conchoidal, and streak grey. Its hardness is 3; its sp. gr. = 2.04. Analysis gave the following figures:—

SiO <sub>2</sub> .	CuO.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	OH <sub>2</sub> .	Mn <sub>2</sub> O <sub>3</sub> .	Total.
31.58	30.28	6.27	0.84	28.71	2.22 =	99.90

Neglecting the manganese and iron, which are probably uncombined, these numbers agree with the formula for asperolite,  $\text{CuSiO}_3 + 3\text{H}_2\text{O}$ , wherein one-third of the copper is replaced by alumina. The dark colour is due to the iron and manganese.

D. A. L.

**The Pegmatite on the Borders of Vizézy, near Montbrison.** By F. GONNARD (*Compt. rend.*, 99, 881—883).—In addition to the minerals already described (this vol., p. 34), the pegmatite near Montbrison contains small, green, hexagonal prisms, truncated at both ends; these, however, are not emeralds, but crystals of green apatite, similar to those found at Irigny and other localities. Notwithstanding the statements of Passiuges and Bournon that this pegmatite contains emeralds and andalusite, the author has not been able to find either of these minerals in it.

C. H. B.

**Diamond-bearing Rocks of South Africa.** By H. E. ROSCOE (*Chem. News*, 50, 243—244).—The diamonds are reached at the Kimberley Mine by shafts sunk through 3 feet of red sand and 5 to 15 feet of tufaceous limestone to a soft, yellow, earthy diamond rock 30 feet thick, succeeded by a soft, blue, diamond rock, proved to a depth of 282 feet. The diamonds are found in the yellow and blue “stuff,” along with garnets, mica, bronzite, ilmenite, pyrites, &c. The following specimens of rocks were examined:—I. A compact greenish-grey rock, labelled “The Hard Rock.” II. A compact rock of dull rusty brown colour, “Layer of Ironstone.” III. A friable earthy rock of greenish-blue colour, in which the diamonds occur. IV. A mixture of several minerals, in pieces about the size of a pea, “Coarse, heavy deposit, Kimberley blue ground.” V. A similar mixture, in much finer grains, labelled “Fine heavy deposit, Kimberley blue ground.” Sections of the first three specimens were cut and sent to Professor Bonuey. An abstract of his report upon them is as follows:—I. This rock is an actinolite-dabase, and could not be distinguished from specimens obtained from various British localities, where rocks of palæozoic or greater age occur. II. This is rather a decomposed basalt belonging to the same group as I, but probably from a different mass, and altered in a different way. These two specimens gave the following results on analysis:—

	I.	II.	III.
SiO <sub>2</sub> .....	58·03	48·47	46·16
Al <sub>2</sub> O <sub>3</sub> .....	15·53	16·33	10·00
Fe <sub>2</sub> O <sub>3</sub> .....	—	9·85	—
FeO .....	9·64	1·65	6·71
MnO .....	4·54	0·48	0·34
CaO .....	6·99	8·43	3·84
MgO .....	4·55	7·38	16·63
Loss on ignition	—	7·44	$\left\{ \begin{array}{l} 5·55 \text{ at } 120^{\circ} \\ 1·89 \text{ ,, red heat} \end{array} \right\}$

	Limonite.	Bronzite.
SiO <sub>2</sub> .....	6·93	55·17
Al <sub>2</sub> O <sub>3</sub> .....	6·85	2·95
Fe <sub>2</sub> O <sub>3</sub> .....	71·40	—
FeO .....	—	5·76
MnO .....	—	—
CaO .....	0·71	3·64
MgO .....	0·86	32·83
H <sub>2</sub> O .....	12·53	—
	99·28	100·35

These have a very similar composition, the second differing from the first in containing a considerable percentage of water, and in the fact that its iron is almost entirely in the peroxidised state. III. Of this specimen, Professor Bonney reports mainly as follows:—No. III is evidently a breccia composed of a compact serpentinous rock of dark colour, the fragments and the paste apparently being similar in character. One or two scales of bronzite and a black mica are scattered in the matrix, with some small grains of a black mineral of irregular fracture, and one of a brown mineral. Microscopic examination shows the ground-mass to consist of a very minute aggregation of doubly refracting crystallites of no very definite but rather fibrous shape, and specks of ferrite. Here and there the colouring mineral is opacite. Frequent cracks appear to traverse the slide, occupied by a clearer mineral similar to that disseminated through the slide. There is a small crystal resembling a hydrous bronzite. He has a very strong suspicion that the fragments have been a basalt-glass, or an olivine-glass, more probably the latter, converted by hydration into a kind of serpentine. An analysis of the earth gave the numbers under III above. It was noticed that a peculiar smell, somewhat like that of camphor, was evolved on treating the soft, blue, diamond earth with hot water. A quantity of the earth treated with ether gave a small quantity of a crystalline, strongly aromatic body, which was very volatile, burned easily with a smoky flame, and melted at about 50°. The presence of this carbonaceous substance is most interesting, and tends to confirm Professor Cohen and Mr. Dunn's hypothesis that the carboniferous shales that are penetrated by the diamond-bearing "pipes" have been the source of the carbon which is now found as diamond. IV and V,

which are samples of the deposit obtained by washing the "stuff," show the minerals which accompany the diamonds. 100 grams of No. V contained:—Garnet 10·76, bronzite 3·64, ilmenite 54·80, pyrites 0·14, mica 0·20, limonite 16·12, pieces of the rock which have escaped disintegration, with some limonite, 10·84, coarse sand, a mixture of all the above, 3·46. The composition of the limonite and bronzite are given above.

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J. T.

## Organic Chemistry.

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**Some Reactions of Silver Cyanide.** By C. L. BLOXAM (*Chem. News*, 50, 155).—Hydrocyanic acid is evolved on treating precipitated silver cyanide with concentrated nitric acid; on boiling, the cyanide is entirely dissolved and silver nitrate crystallises from the cooled solution. If, however, the solution is decanted when only a portion of the precipitate is dissolved, it deposits minute needles as it cools; these crystals, which mat together in a remarkable manner when the solution is stirred, are silver nitrocyanoide,  $\text{AgCN} \cdot 2\text{AgNO}_3$  (Abstr., 1884, 168). The residue left by the nitric acid consists of unattacked cyanide mixed with some of these crystals. This change also takes place slowly in the cold with concentrated nitric acid; a boiling mixture of nitric acid, sp. gr. 1.400, with an equal volume of water, appears to be the most suitable for dissolving silver cyanide as nitrocyanoide.

When precipitated silver cyanide is treated with a strong solution of sodium carbonate, it becomes granular, and the granules are observed to be fringed with minute needles. By boiling the precipitated cyanide with strong solutions of potassium or of sodium carbonate, it dissolves practically without decomposition, but is converted into small prismatic crystals, which are sparingly soluble in the hot solution of the alkaline carbonate, and are completely deposited from this solution as it cools. D. A. L.

**Action of Primary Alcoholic Iodides on Silver Fulminate.** By G. CALMELS (*Compt. rend.*, 99, 794—797).—25 grams of dried silver fulminate were heated with 25 grams of methyl iodide and 40 grams of ether in a sealed tube at  $50^\circ$  for 24 hours. The products are silver iodide, methylcarbylamine, and  $\beta$ -nitroethylene. Ethyl iodide and the higher primary iodoparaffins react in a precisely similar manner:  $\text{CNAg} : \text{CAgNO}_2 + 2\text{MeI} = 2\text{AgI} + \text{CNMe} + \text{CH}_2 : \text{CH.NO}_2$ . In this reaction silver fulminate is split up into two parts. In order if possible to obtain the intermediate compounds—



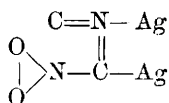
100 grams of methyl iodide mixed with 50 grams of ether were allowed to act on 50 grams of the dried fulminate at the ordinary

temperature for four or five days, but the only products obtained were  $\alpha$ -nitroethylene and methylcarbylamine. Ethyl iodide and its higher homologues behave in the same way.

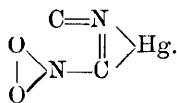
The nitro-derivatives of the ethylene series are characterised by their power of existing in two modifications, the  $\alpha$ -derivatives forming colourless liquids soluble in ether and chloroform, whilst the  $\beta$ -derivatives are yellow resinous solids insoluble in the same solvents. From their chemical behaviour, it would seem that the former are the true nitro-derivatives, whilst the latter are oximido-derivatives.

From these results, it follows that silver fulminate contains two dissymmetrical groups, each of which contains one atom of silver. One of these groups is silver cyanide,  $\text{CNAg}$ , whilst the other

contains the sub-group  $\text{N} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$  and the second atom of silver, the latter being united with the second atom of carbon, which is in direct union with the nitrogen in the first group (this nitrogen acting as a pentad) and thus links the two groups together:—



Silver fulminate.



Mercuric fulminate.

It is evident from this formula that the two metallic atoms in the silver fulminate have different functions, and this explains the non-existence of mixed fulminates of the alkali metals. The formula also explains generally the observed action of the halogens on the fulminates.

The fulminates are isocyanides or metallic carbylamines united by nitrogen to a bivalent residue of a metallic derivative of nitromethane, the metal attached to the nitro-group being any metal whatever. This function, which is peculiar to the carbylamines and does not appertain to the metallic nitriles (cyanides), may be termed the carbazilic function. The relation of the carbazilic type to the allied types is shown by the following formulæ:—



Nitrile.



Metanitrile.



Carbylamine.



Carbazilic.

C. H. B.

**Gallisin.** By C. SCHMITT and J. ROSENHEK (*Ber.*, **17**, 2456—2467).—This paper forms a continuation of C. Schmitt and A. Cobenzl's communication on this subject (*Abstr.*, 1884, 961).

*Action of Sulphuric Monochloride on Gallisin.*—When pure dry gallisin is gradually added to sulphuric monochloride,  $\text{SO}_2\text{Cl.OH}$ , it is dissolved, hydrochloric acid being at the same time copiously evolved. All heating must be carefully avoided, as decomposition sets in at about  $60\text{--}70^\circ$ . The syrup produced could not be obtained in a crys-

talline state, and as it is decomposed even at ordinary temperatures it was poured on to broken ice, and the aqueous solution thus obtained neutralised with barium carbonate. The barium salt was obtained as a white flocculent precipitate by pouring its solution into alcohol; when dried, it forms a white hygroscopic powder which is slowly decomposed on exposure to the air, quickly at 80—100°. The composition of this substance is  $C_6H_8O_{18}S_4Ba_2 + 5H_2O$ , and it appears to be identical with Claesson's barium dextrosotetrasulphate (Abstr., 1879, 1033). The authors found the rotation of this barium salt in aqueous solution to be 52°, Claesson obtaining 51° for his compound. If this is really identical with Claesson's compound, the non-crystallising of the chloride first formed is probably due to the presence of impurities.

*Action of Bromine on Gallisin.*—30 grams of gallisin were dissolved in  $1\frac{1}{2}$  litres of water, and heated for about six hours in a well-corked champagne bottle in the water-bath, bromine being added at intervals. Altogether 75 grams of bromine were used. The pressure generated was considerable, and the odour of bromoform was perceptible each time the bottle was heated. The authors were unable to isolate the unstable brominated compound which is formed, and the product was therefore treated with silver oxide. The silver compound was also very unstable and was at once decomposed with sulphuretted hydrogen. The free acid could not be obtained in a crystalline or pure form. It is dextrorotary, but unlike other acids obtained in a similar manner, it gives a precipitate with lead salts. If added to a solution of ferric chloride (even in small quantities), it prevents the precipitation of ferric hydroxide by ammonia. It reduces Fehling's and Knapp's solutions. When neutralised with calcium, barium, or cadmium carbonates, it yields uncrystallisable salts which are precipitated by alcohol. None of the compounds could be obtained in a pure or definite state.

*Dry Distillation of Gallisin with Lime.*—The distillate separated into two layers. The aqueous layer contained acetic acid and acetone; the oily layer boiled at 82—86° and is probably Fremy's metacetone.

*Action of Pancreatic Juice on Gallisin.*—If gallisin is treated with pancreatic juice and the whole allowed to remain for a considerable time in a warm room, the former is converted into a substance capable of undergoing alcoholic fermentation with yeast: the quantity converted is dependent on the length of time during which the pancreatic juice is allowed to act, but the authors have not yet been able to convert the whole of the gallisin into such fermentable substance.

*The Specific Rotary Power of Pure Gallisin,* in aqueous solution, increases approximately in proportion to the increase in quantity of the solvent.

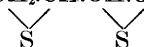
*Analysis of Commercial Glucose and Quantitative Estimation of Gallisin therein.*—Neubauer states that gallisin does not reduce Fehling's solution, and this statement has been generally accepted as correct. The authors find that gallisin *does* reduce Fehling's solution, 1.0978 grams gallisin requiring 100 c.c. of solution. The authors



suggest the following as the best method of estimating pure gallisin and pure glucose in the commercial article. A solution is made containing less than 1 per cent., and is titrated with Fehling's solution. Another solution is made, fermented with yeast, and then titrated. The latter titration gives the quantity of gallisin present, and the difference between the two, the quantity of pure glucose.

L. T. T.

**Thiovaleraldehyde.** By G. A. BARBAGLIA (*Ber.*, 17, 2654—2655).—In a previous paper (*Abstr.*, 1881, 34), the author showed that sulphur reacted with valeraldehyde at about 250° according to the equation  $4C_5H_{10}O + S_2 = 2C_5H_{10}S + 2C_5H_{10}O_2$ . He finds that secondary reactions also take place which give rise to the formation of : 1, hydrogen sulphide, the quantity of which increases as the temperature is raised ; 2, a heavy red-coloured liquid, distilling between 200° and 300°, and having an offensive odour recalling that of onions and putrid eggs, the quantity of this substance being greater the larger the amount of sulphur employed ; 3, *trithiovaleraldehyde*,  $CH_2.CH.CH.CH.CHS$ ,



crystallising in bright yellow silky prisms melting at 94·5°; it is insoluble in water, very readily soluble in ether and alcohol.

A. K. M.

**Aldehyde and Ethylidene Derivatives. Value of the Carbonyl Affinities of Carbon.** By R. RÜBENCAMP (*Annalen*, 225, 267—290).—The liquid boiling about 85°, which Wurtz (*Jahresbericht*, 1856, 597) and Bachmann (*Annalen*, 218, 42) considered to be methyl ethyl acetal, is in reality a mixture of dimethyl acetal and diethyl acetal. The author regards the existence of the mixed acetals as very doubtful.

*Ethylidene diacetate* is formed by the action of silver acetate on ethylidene acetochlorhydrin diluted with absolute ether; the properties of this body have been previously described by Franchimont. By a similar reaction, *ethylidene dipropionate*,  $C_2H_4(C_3H_5O_2)_2$ , and other analogous compounds can be prepared. The physical properties of these bodies are shown in the following table :—

	B. p. (corr.).	Sp. gr. at 15°.	Index of refraction at 28·2.
Ethylidene diacetate . . . . .	168·4	1·073	1·399
„ acetopropionate . . . . .	178·6	1·044	1·402
„ dipropionate . . . . .	192·2	1·020	1·407
„ acetobutyrate . . . . .	192·6	1·014	1·4065
„ dibutyrate . . . . .	215·5	0·9855	1·411
„ acetovalerate . . . . .	194·199	0·991	1·408
„ divalerate . . . . .	225	0·947	1·414
„ propiochlorhydrin . . . . .	135 (uncor.)	1·071	—
„ butyrochlorhydrin . . . . .	149 „	1·038	—
„ valerochlorhydrin . . . . .	162	0·997	—

As the compound produced by the action of silver propionate on ethylidene acetochlorhydrin is identical with the compound obtained

by the action of silver acetate on ethylidene propiochlorhydrin, and in like manner, as the body produced from silver acetate and ethylidene butyrochlorhydrin is identical with that obtained from silver butyrate and ethylidene acetochlorhydrin, the author concludes that both the "carbonyl affinities" are of equal value.

W. C. W.

**Some Reactions of Carbon Bisulphide, and its Solubility in Water.** By G. CHANCEL and F. PARMENTIER (*Compt. rend.*, **99**, 892—894).—When baryta-water is mixed with an aqueous solution of carbon bisulphide, or with a mixture of carbon bisulphide and water, very little action takes place at the ordinary temperature, but if the mixture is heated an abundant precipitate of barium carbonate is formed, and the supernatant liquid becomes yellow. If the mixture is heated in sealed tubes at 100° for some time, the liquid gradually becomes colourless, and the amount of barium carbonate formed is greater than that calculated from the equation given by Berzelius,  $3\text{CS}_2 + 6\text{MOH} = \text{M}_2\text{CO}_3 + 2\text{M}_2\text{CS}_3 + 3\text{H}_2\text{O}$ .

Experiments made by heating known weights of carbon bisulphide with an excess of a somewhat dilute solution of barium hydroxide at 100°, in sealed tubes previously filled with nitrogen, show that under these conditions the reaction is accurately represented by the equation  $\text{CS}_2 + 2\text{BaH}_2\text{O}_2 = \text{BaCO}_3 + \text{BaS}_2\text{H}_2 + \text{H}_2\text{O}$ . If the mixture is heated in contact with air, the same proportion of barium carbonate is formed, but it is mixed with a certain quantity of barium sulphate formed by the oxidation of the hydrosulphide.

The authors have employed this reaction to determine the amount of carbon bisulphide dissolved by water at different temperatures, with the following results:—

Temperature .....	3·4°	15·8°	30·1°	41·0°
CS <sub>2</sub> in grams per litre ...	2·00	1·81	1·53	1·05

The solubility diminishes rapidly above 30°, and becomes *nil* at the boiling point of the bisulphide. The solution of carbon bisulphide behaves under changes of temperature in the same way as the solution of a gas.

C. H. B.

**Normal  $\alpha$ -Hydroxyvaleric Acid.** By W. JUSLIN (*Ber.*, **17**, 2504—2506).—Hitherto Pinner and Bischoff's trichlorovalerolactic acid was the only known derivative of the above acid. The author has now prepared the unsubstituted acid by the action of alkalis on monobromovaleric acid, and also by the action of hydrocyanic acid and hydrochloric acid on butaldehyde. The valeric acid employed was obtained by heating propylmalonic acid. *Ethyl  $\alpha$ -bromovalerate* is a colourless liquid of pleasant odour. It boils at 190—192°, and has a sp. gr. of 1·226 at 18° compared with water at 4°. This ether was then digested on the water-bath with a solution of sodium hydroxide, the product evaporated to dryness, treated with sulphuric acid, and extracted with ether. On evaporation, the ether left  *$\alpha$ -hydroxyvaleric acid* as a syrup which, in a vacuum, solidified to large tabular crystals. It is very deliquescent and melts at 28—29°. The *barium salt* forms

glistening scaly crystals soluble in water; the bluish-green *copper salt* is sparingly soluble in water.

*Butaldehyde* was prepared by the dry distillation of a mixture of calcium butyrate and formate, and was converted into its *hydrogen sodium sulphite compound*. This substance forms long silky crystals easily soluble in water, sparingly so in alcohol and insoluble in ether; it was distilled with a concentrated solution of sodium hydroxide, and the butaldehyde thus obtained heated with hydrocyanic acid in closed tubes at 70°. The nitrile was then boiled with fuming hydrochloric acid, the excess of the latter acid evaporated off, and the residue extracted with ether. On evaporating the ethereal solution, an insoluble oil was left, which proved to be the anhydride of the hydroxy-acid. This was reconverted into the acid by boiling with potash, &c., and the acid thus obtained was found to be identical with that prepared with  $\alpha$ -bromovaleric acid. When kept in a desiccator, the hydroxy-acid is gradually converted into the anhydride.

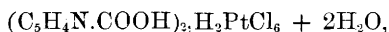
L. T. T.

**Acetonedicarboxylic Acid.** By H. v. PECHMANN (*Ber.*, 17, 2542—2543).—Citric acid is heated with sulphuric acid on the water-bath until the carbonic oxide evolved is accompanied by carbonic anhydride, and the whole then cooled and water added. *Acetonedicarboxylic acid*,  $\text{CO}(\text{CH}_2\text{COOH})_2$ , crystallises out in colourless needles. This substance forms a compound with phenylhydrazine. When heated alone, it is decomposed into carbonic anhydride and acetone. The melting point is about 138°. The same decomposition takes place when the acid is heated with acids or alkalis, or its aqueous solution is boiled. The ethers of this acid are liquid, and the author is now investigating their substitution products.

L. T. T.

**Amides of Citric Acid and their Conversion into Pyridine-derivatives.** By A. BEHRMANN and A. W. HOFMANN (*Ber.*, 17, 2681—2699).—*Citramide*,  $\text{C}_6\text{H}_5\text{O}_4(\text{NH}_2)_3$ , is readily obtained by the action of very strong aqueous ammonia on trimethyl citrate at the ordinary temperature. If alcoholic ammonia is employed, the action is much slower and the yield much smaller. It is sparingly soluble in cold, readily in hot water, and insoluble in alcohol and ether; when heated above 200°, it begins to turn brown, and at 210—215° it melts to a black liquid. It yields no acetic derivative when treated either with acetic chloride or acetic anhydride. If the mother-liquor from the citramide is evaporated to a syrup, acidulated with nitric acid, and alcohol and ether then added, *citrodiamic acid*,  $\text{C}_6\text{H}_5\text{O}_4(\text{NH}_2)_2\text{OH}$ , separates; this crystallises in white scales melting at 158°, is readily soluble in water and almost insoluble in alcohol and ether. The silver salt,  $\text{C}_6\text{H}_5\text{O}_4(\text{NH}_2)_2\text{OAg}$ , forms a crystalline powder sparingly soluble in water; the lead and other salts are soluble. If the syrupy mother-liquor from the citramide is treated with ammonia and silver nitrate, *argentic citramonamate*,  $\text{C}_6\text{H}_5\text{O}_4(\text{NH}_2)(\text{OAg})_2$ , is precipitated as a yellowish-white powder. The free acid is extremely soluble in water, less so in alcohol, and is insoluble in ether and light petroleum; it melts at 138°. A better yield of the citramic acids is obtained by treating citramide with weaker ammonia.

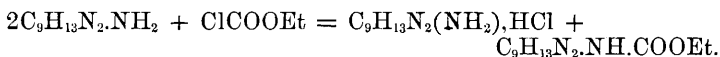
*Citrazinic acid*,  $C_6H_5NO_4$ : citramide is treated with 4—5 parts of sulphuric acid (70—75 per cent.), the mixture heated at about  $130^\circ$ , and the solution poured, after cooling, into 2 to 3 vols. water; the acid then separates as a yellowish powder. It may also be obtained by the action of sulphuric acid on the citramic acids. Citrazinic acid is very sparingly soluble even in boiling water and insoluble in other neutral liquids; boiling concentrated hydrochloric acid dissolves it sparingly, but it is soluble in warm concentrated sulphuric acid, and very readily in alkalis and alkaline carbonates. The solutions of the citrazinates assume a greenish-blue coloration on exposure to the air, the ammoniacal solution becoming deep blue like an ammoniacal copper solution; the addition of an acid destroys the colour immediately. When citrazinic acid is added to a hot neutral solution of potassium or sodium nitrite, a deep blue coloration is immediately produced. Citrazinic acid is very stable, and may be heated to  $275^\circ$  without decomposition; it carbonises above  $300^\circ$  without melting. It may be boiled for hours with the strongest alkalis without yielding a trace of ammonia, but is decomposed by fusion with alkalis with formation of potassium cyanide. The alkali salts are very soluble, the barium and calcium salts sparingly so; the lead salt forms a yellowish, the copper salt a brown, and the silver salt a yellow precipitate. The *methyl salt*,  $C_6H_4MeNO_4$ , forms lustrous scales, which are sparingly soluble in water, alcohol, and ether; the *ethyl salt*,  $C_6H_4MeNO_4$ , has similar properties. A *diacetyl-derivative*,  $C_8H_3Ac_2NO_4$ , may be obtained by dissolving the acid in boiling acetic anhydride; it is readily decomposed by water or alcohol. When citrazinic acid is boiled with tin and hydrochloric acid, tricarballic acid is produced:  $C_6H_5NO_4 + 2H_2O + H_2 = C_6H_8O_6 + NH_3$ . The authors think it very probable that citrazinic acid is a dihydroxy-pyridinecarboxylic acid,  $C_5H_2(OH)_2N.COOH$ . When it is heated with phosphorous pentachloride and oxychloride at  $250^\circ$ , and the product treated with boiling water, a dichloropyridinecarboxylic acid,  $C_5H_2Cl_2N.COOH$ , is obtained, melting at  $210^\circ$ ; this is sparingly soluble in water, moderately in cold, readily in boiling alcohol, and extremely soluble in ether; it is insoluble in hydrochloric acid, but dissolves in warm concentrated sulphuric acid, and readily in all alkaline liquids. The silver salt,  $C_5H_2Cl_2N.COOAg$ , crystallises from boiling water in magnificent colourless needles. By the action of hydriodic acid on the chlorinated acid, a *pyridinecarboxylic acid* is obtained, which melts at  $306^\circ$ , and is identical with Skraup's  $\gamma$ -pyridinecarboxylic acid (*Ber.*, **12**, 2332) and Weidel's isonicotinic acid. It is sparingly soluble in cold, more readily in hot water, sparingly also in alcohol and ether; the alkali salts are soluble, the silver salt insoluble; the copper salt forms a bluish-green crystalline precipitate; the platinumchloride,



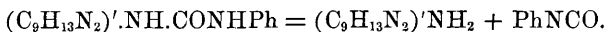
crystallises in thick orange-yellow prisms. If, in the reduction of dichloropyridinecarboxylic acid, as above, phosphorus be added, the carboxyl-group is reduced to methyl, and *parapicoline* is obtained.

A. K. M.

**Action of Ethyl Chlorocarbonate on Nitrogenous Organic Compounds.** By E. v. MEYER (*J. pr. Chem.*, **30**, 115—125).—Ethyl chlorocarbonate reacts with cyanethine, forming *cyanethine hydrochloride* and *ethyl cyanethine carboxylate*, thus:



This latter compound can be separated from the hydrochloride by treatment with benzene, which dissolves the ethyl cyanethine carboxylate. It is an easily fusible solid, boils at  $247^\circ$ , its aqueous solution has an intensely bitter taste and an alkaline reaction, and by continued boiling is resolved into carbonic anhydride, ethyl alcohol, and cyanethine. *Ethyl cyanethine-carboxylate* is easily dissolved by acids, and is reprecipitated from these solutions by bases; its solutions are precipitated by several metallic salts, such as mercuric chloride, gold chloride, and silver nitrate. This compound may also be regarded as a derivative of ethyl carbamate, and is, in fact, *ethyl cyanoconyl-carbamate*,  $(\text{C}_9\text{H}_{13}\text{N}_2)'\text{HN}\cdot\text{COOEt}$ . With ammonia it forms *cyanethine-carbamide*,  $\text{C}_9\text{H}_{13}\text{N}_2\cdot\text{NH}\cdot\text{CONH}_2$ , and with aniline *cyanethine-carbanilide*,  $(\text{C}_9\text{H}_{13}\text{N}_2)'\cdot\text{NH}\cdot\text{CONHPh}$ . This latter compound crystallises from alcohol in long, silky needles, melting at  $184^\circ$ , it is a very stable compound, and unaffected by acids or bases. When heated in a current of hydrochloric acid gas, it is resolved into cyanethine and phenyl cyanate, thus:—



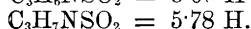
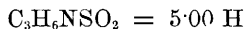
*Cyanethine-carbanilide* is formed also by the direct union of phenyl cyanate and cyanethine, a formation analogous to that of methyl-phenylcarbamide from methylamine and phenyl cyanate.

The “*oxybase*,”  $\text{C}_9\text{H}_{12}\text{N}_2\cdot\text{OH}$ , obtained from cyanethine, reacts with ethyl chlorocarbonate, forming a compound similar to that obtained from cyanethine; it is a liquid which is decomposed by boiling with mineral acids into carbonic anhydride and salts of the “*oxybase*.”

Cyanethine heated with acetic oxide at  $170^\circ$  is converted into *acetylcyanethine*,  $(\text{C}_9\text{H}_{13}\text{N}_2)\cdot\text{NHAc}$ , a crystalline compound melting at  $59^\circ$ , and but sparingly soluble in water.

Acetamide, benzamide, and acetanilide yield no ethyl carboxylates when treated with ethyl chlorocarbonate. Quinoline yields the hydrochloride of ethylquinoline. P. P. B.

**Cystine.** By E. KÜLZ (*Zeit. Biol.*, **20**, 1—10).—The author found 5.33 per cent. H, as the mean of several analyses of pure crystallised cystine, and consequently assigns the formula  $\text{C}_3\text{H}_6\text{NSO}_2$ , instead of the  $\text{C}_3\text{H}_2\text{NSO}_2$  given by Hoppe-Seyler and others.



The rotatory power when dissolved in ammonia is  $[\alpha]_D = -142^\circ$ , using a Jellet-Cornu apparatus; Mauthner found  $-205.88^\circ$ ; this difference is, however, accounted for by the fact that Mauthner dissolved his crystals in hydrochloric acid. J. P. L.

**Preparation of Pure Thiophene.** By V. MEYER (*Ber.*, 17, 2641—2643).—If in extracting thiophene from its mixture with benzene the proportion of sulphuric acid be diminished, thiophene alone is taken up, and may be recovered in a state of purity by distilling the sulphonic acid. 2000 kilos. coal-tar benzene were treated with 100 kilos. sulphuric acid, the product converted into lead salt, and this distilled with ammonium chloride. The amount of thiophene obtained was 1944 grams. The acid layer obtained after shaking with sulphuric acid should be at once diluted with water to prevent carbonisation. To obtain 100 per cent. thiophene, 400 kilos. benzene are agitated for two hours with 16 kilos. sulphuric acid, the product converted into the lead salt, then into the ammonium salt, and this submitted to distillation. A. K. M.

**Nitration of Thiophene.** By V. MEYER and O. STADLER (*Ber.*, 17, 2648—2650).—The nitration of thiophene may be effected by passing air saturated with its vapour through fuming nitric acid, when after some hours the liquid separates into two layers. On pouring the product into water, a heavy oil separates. The mono- and di-nitrothiophene obtained may be separated either by steam distillation or by fractional distillation. *Mononitrothiophene*,  $C_4H_3S.NO_2$ , more closely resembles paranitrotoluene than nitrobenzene; it is of a pale yellow colour, solidifies in large prisms after fusion, has an odour like that of bitter almond oil; it melts at  $44^\circ$ , boils at  $224\text{--}225^\circ$  (corr.), and becomes red on exposure to light. It is insoluble in alkalis, and is converted by nitric acid into dinitrothiophene. Nitrothiophene gives no reaction with isatin and sulphuric acid. *Dinitrothiophene*,  $C_4H_2S(NO_2)_2$ , crystallises from alcohol in yellow scales, moderately soluble in hot water, and is decomposed by alkalis with red coloration. It melts at  $52^\circ$ , is somewhat volatile in steam, and boils at about  $290^\circ$  without much decomposition. Metadinitrobenzene boils at  $297^\circ$  (corr.). An isomeric dinitrothiophene is also obtained which melts at  $75\text{--}76^\circ$ , crystallises in needles, and is somewhat more volatile in steam. A. K. M.

**Acetothiënone and some of its Derivatives.** By A. PETER (*Ber.*, 17, 2643—2647).—*Acetothiënone*,  $C_4H_3S.COMe$ , is best prepared by the action of aluminium chloride on a solution of 10 grams thiophene (98 per cent. thiophene) and 9.1 grams acetic chloride in 50 grams light petroleum. When the reaction is ended, the petroleum is poured off, and the product warmed and poured into water. After purification, acetothiënone is a colourless oil boiling at  $213.5^\circ$  (corr.), and remaining liquid at  $-15^\circ$ ; it has an odour closely resembling that of acetophenone; its sp. gr. is 1.167 at  $24^\circ$ . When a trace of it is heated with isatin and sulphuric acid, it yields the indophenine-blue colour. *Thiënylmethylacetoxime*,  $C_4H_3S.CMe:NOH$ , obtained from acetothiënone and hydroxylamine, forms a white crystalline mass, melts at about  $110^\circ$ , and gives no characteristic reaction with isatin and sulphuric acid. *Acetothiënonephenylhydrazine*,  $C_4H_3S.CMe:NO.NHPh$ , is prepared by heating an aqueous solution of acetothiënone, phenylhydrazine hydrochloride, and sodic acetate, and

crystallises from alcohol in clusters of bright yellow needles melting at  $96^{\circ}$ . On oxidising acetothiënone with alkaline potassium permanganate solution, a thiophenic acid,  $C_4H_3S.COOH$ , is obtained melting at  $124.5^{\circ}$ ; it yields the indophenine colour-reaction with isatin and sulphuric acid. Its identity with  $\alpha$ - or  $\beta$ -thiophenic acid is not yet established. By the nitration of acetothiënone at  $-8^{\circ}$ , two isomeric mononitro-derivatives are obtained, one crystallising in long yellow four-sided vitreous prisms melting at  $122.5^{\circ}$ , the other in small lustrous scales melting at  $86^{\circ}$ .

A. K. M.

### Decomposition of Benzonitrile by Fuming Sulphuric Acid.

By A. PINNER (*J. pr. Chem.*, **30**, 125—127).—A reply to Gumpert's remarks (this vol., p. 52) on the preparation of cyanphenine. The author shows that Gumpert employed a method different from that used by Klein and himself (*Ber.*, **11**, 764), and cites further experiments to show that cyanphenine is obtained on adding benzonitrile to a large excess of sulphuric acid.

P. P. B.

**Dinitrotoluene.** By W. STAEDEL (*Annalen*, **225**, 384—388).—The dinitrotoluene melting at  $60^{\circ}$  which the author obtained from Tiemann's dinitrotoluidine melting at  $168^{\circ}$  (*Annalen*, **217**, 205), is shown to have the constitution  $C_6H_3Me(NO_2)_2$  [ $Me : NO_2 : NO_2 = 1 : 2 : 6$ ] by the following facts. On reduction with ammonium sulphide, the dinitrotoluene yields a nitrotoluidine melting at  $90^{\circ}$ . Phthalyl orthotoluide melting at  $180^{\circ}$  forms two isomeric nitro-products, which are converted by the action of alcoholic ammonia into nitrotoluidines melting at  $90^{\circ}$  and  $109^{\circ}$  respectively. Nitrotoluidine (melting at  $90^{\circ}$ ) from dinitrotoluene (melting at  $60^{\circ}$ ), or from phthalyl orthotoluide, can be converted into orthonitrotoluene, and the nitrotoluidine melting at  $109^{\circ}$ , from phthalyl orthotoluide, yields paranitrotoluene. The constitution of the following bodies has now been ascertained.

	M. p.		
Trinitrotoluene ..	$81^{\circ}$	$C_6H_3MeNO_2NO_2NO_2$	1 : 2 : 4 : 6
Dinitrotoluidine .	168	$C_6H_2MeNO_2NH_2NO_2$	1 : 2 : 4 : 6
Dinitrotoluene...	60	$C_6H_3MeNO_2NO_2$	1 : 2 : 6
Nitrotoluidine ...	90	$C_6H_3MeNH_2NO_2$	1 : 2 : 6
„ ...	109	$C_6H_3MeNH_2NO_2$	1 : 2 : 4

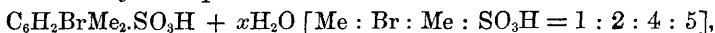
W. C. W.

**Bromo-substitution Derivatives of Orthoxylene.** By O. JACOBSEN (*Ber.*, **17**, 2372—2379).—The only halogen derivatives of orthoxylene previously described are those in which substitution occurs in the side-chains; the present paper describes bromine derivatives obtained by bromination in the cold in which substitution occurs in the benzene-ring.

*Monobromorthoxylene*,  $C_6H_3MeMeBr$  [1 : 2 : 4] is obtained by the action of bromine in presence of iodine on commercial orthoxylene in the cold, but is contaminated with bromoparaxylene and bromometaxylene. Its purification is effected by conversion into the sulphonic acids and crystallisation of the barium salts, when the ortho-derivative separates in large crystals, and is readily separated mechanically from the meta- and para-salts. Monobromoxylene is

regenerated from the barium sulphonate by converting it into the sodium salt and heating this with concentrated hydrochloric acid at 200°. It is liquid, but solidifies below 0° to a fibrous crystalline mass, melts at  $-0.2^\circ$ , boils at 214.5 under 760 mm. pressure, and has a sp. gr. of 1.3693 at  $\frac{15^\circ}{15^\circ}$ . Heated with ethyl chlorocarbonate and sodium amalgam, it is converted into paraxylic acid, showing that the bromine is in the para-position.

*Bromorthoxylenesulphonic acid*,



is obtained by dissolving bromorthoxylylene in weak Nordhausen sulphuric acid; it forms a fibrous crystalline mass, very readily soluble in water, very sparingly soluble in cold dilute sulphuric acid. Its constitution is shown by the action of sodium amalgam on the sodium salt, when it yields sodium orthoxylylene sulphonate [1 : 2 : 5]. The *barium* salt,  $(\text{C}_6\text{H}_2\text{BrMe}_2\text{SO}_3)_2\text{Ba} + 3\text{H}_2\text{O}$ , crystallises in long hard prisms, and is very sparingly soluble in cold water. The *sodium* salt,  $\text{C}_6\text{H}_2\text{Br}.\text{SO}_3\text{Na} + 1\frac{1}{2}\text{H}_2\text{O}$ , crystallises in very long, slender needles, sparingly soluble in cold, very readily soluble in hot water. The *potassium* salt,  $\text{C}_6\text{H}_2\text{Br}.\text{SO}_3\text{K} + \text{H}_2\text{O}$ , forms thin glassy prisms, moderately soluble in cold water. By fusion with potash, the sulphonic acid is split up into a variety of products, of which the only one that could be isolated was  $\beta$ -metabromosalicylic acid, and this only in very minute quantity.

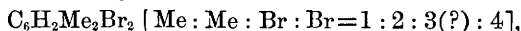
*Bromorthoxylenesulphonamide*,  $\text{C}_6\text{H}_2\text{Br}.\text{SO}_2\text{NH}_2$ , crystallises in long hairlike needles, melts at  $213^\circ$ , is sparingly soluble in water and cold alcohol, moderately soluble in hot alcohol.

*Bromorthotoluic acid*,  $\text{C}_6\text{H}_3\text{MeBr}.\text{COOH}$  [Me : COOH : Br = 1 : 2 : 4], is prepared by boiling bromorthoxylylene with dilute nitric acid (1 : 5) in a reflux apparatus. It crystallises in stellate groups of needles, melts at  $174-176^\circ$ , is sparingly soluble in cold, readily soluble in hot water, soluble in alcohol. The *calcium* salt crystallises with 2 mols.  $\text{H}_2\text{O}$  in small hard prisms. When fused with potash, the acid yields parahomometahydroxybenzoic acid.

*Dibromorthoxylenes*.—By the action of bromine on pure bromorthoxylylene in presence of iodine, two dibromo-compounds are formed, and can be separated by crystallisation from alcohol, one only being solid at ordinary temperatures.

*Solid dibromorthoxylylene*,  $\text{C}_6\text{H}_2\text{MeMeBrBr}$  [1 : 2 : 4 : 5], is formed in by far the largest quantity; it crystallises in large rhombic tables or long needles, is sparingly soluble in cold, readily in hot alcohol and hot glacial acetic acid, melts at  $88^\circ$ , sublimes slowly at a little above the melting point in large thin plates, and boils at  $278^\circ$ . Heated with methyl iodide and sodium, it yields durenene together with some pseudocumene and regenerated orthoxylylene.

*Liquid dibromorthoxylylene*,



solidifies on cooling to a hard crystalline mass, melts at  $+6.8^\circ$ , boils at  $277^\circ$ , and has a sp. gr. of 1.7842 at  $\frac{15^\circ}{15^\circ}$ . The endeavour to deter-



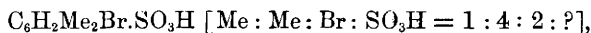
mine its constitution by replacing bromine by methyl groups did not lead to satisfactory results; the action could only be started by repeated additions of ethyl acetate, but much orthoxylylene was then regenerated; neither isodurene nor pseudocumene were formed. It is probable that this compound corresponds with the still unknown [1 : 2 : 3 : 4] tetramethylbenzene.

All attempts to prepare a pure tribromorthoxylylene were unsuccessful, although by the action of bromine on solid dibromorthoxylylene in presence of iodine and a little glacial acetic acid a very small quantity of a substance crystallising in needles and melting at 50–60° was obtained; this appeared to be an impure tribromo-derivative. The end-product of the action of bromine on orthoxylylene in the cold is *tetrabromorthoxylylene*,  $C_6Me_2Br_4$ . It crystallises in long needles, melts at 262°, and distils unchanged at a very high temperature, is sparingly soluble even in boiling alcohol, but is readily soluble in hot benzene.

*Mercury diorthoxylene*,  $MeMeC_6H_4.Hg.C_6H_4.MeMe$ , is obtained as a bye-product in the action of sodium amalgam and ethyl chlorocarbonate on bromorthoxylylene. It crystallises in long, slender needles, melts at 150°, can be in great part distilled unchanged by careful heating, and is sparingly soluble in ether and alcohol, readily in chloroform, carbon bisulphide, benzene, &c.

Pure monobromoparaxylylene does not solidify at  $-15^\circ$ , and boils at  $205.5^\circ$  under 755 mm. pressure. This differs from the figures given by Jannasch (this Journal, 1874, 468) of  $+10^\circ$  for the melting point, and  $199.5$ – $200.5^\circ$  for the boiling point, but is in agreement with the earlier statement of Fittig and Jannasch (*Annalen*, **151**, 283).

*Bromoparaxylenesulphonic acid*,



crystallises in nacreous plates or flat needles. The *sodium* salt,  $C_6H_2Br.SO_3Na + H_2O$ , crystallises in long thin prisms or in rhombic or hexagonal tables. The *barium* salt crystallises in thin hexagonal plates, or small prisms, and is sparingly soluble in hot water.

*Bromoparaxylenesulphonamide*,  $C_6H_2Me_2Br.SO_2NH_2$ , crystallises in flat prisms, melts at  $206^\circ$ , is sparingly soluble in cold, readily soluble in hot water.

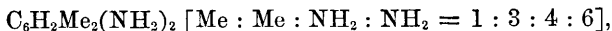
A. J. G.

**Nitro- and Amido-derivatives of Metaxylylene.** By E. GREVINGK (*Ber.*, **17**, 2422–2431).—*Consecutive metadininitrometaxylylene*,  $C_6H_2Me_2(NO_2)_2$  [Me :  $NO_2$  : Me :  $NO_2 = 1 : 2 : 3 : 4$ ], is obtained together with the symmetrical dinitrometaxylylene melting at  $93^\circ$  previously described by Fittig (*Annalen*, **147**, 17, and **148**, 5), by treating metaxylylene with a mixture of sulphuric and nitric acids at a temperature of  $3$ – $6^\circ$ . It crystallises in plates, melts at  $82^\circ$ , and is more readily soluble in alcohol and glacial acetic acid than the other modification. On nitration, both the diinitro-compounds are converted into the trinitrometaxylylene [Me :  $NO_2$  : Me :  $NO_2$  :  $NO_2 = 1 : 2 : 3 : 4 : 6$ ], melting at  $176^\circ$ , described by Fittig (*loc. cit.*).

*Consecutive metanitroxylidine*,  $C_6H_2Me_2(NH_2).NO_2$ , is obtained by the reduction of consecutive dinitrometaxylylene with hydrogen sulphide

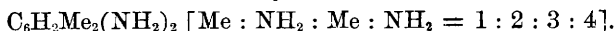
in alcoholic ammoniacal solution. It crystallises in golden-yellow needles, melts at  $78^{\circ}$ , and is soluble in water, alcohol, and light petroleum. The *acetyl* derivative crystallises in white needles and melts at  $149^{\circ}$ . The *acetyl* derivative prepared from the nitroxylidene of melting point  $123^{\circ}$ , derived from symmetrical dinitrometaxylene, also crystallises in white needles, but melts at  $159$ — $160^{\circ}$ .

*Symmetrical metadiamidometaxylene,*



is prepared by reduction of the corresponding nitroxylidene (melting at  $123^{\circ}$ ) with stannous chloride and hydrochloric acid. After being purified by sublimation, it forms snow-white crystals, and melts at  $104^{\circ}$ . The hydrochloride yields Bismarck brown with sodium nitrate, and a chrysoidine with diazobenzene chloride, showing the base to be a metadiamine.

*Consecutive metadiamidometaxylene,*



The reduction of 1 : 2 : 3 : 4 nitroxylidene cannot be effected by stannous chloride, tin and hydrochloric acid have therefore to be used. The diamine forms fine white crystals, and gives the colour reactions of a metadiamine.

*Triamidometaxylene*,  $\text{C}_6\text{HMe}_2(\text{NH}_2)_3 [\text{Me} : \text{NH}_2 : \text{Me} : \text{NH}_2 : \text{NH}_2 = 1 : 2 : 3 : 4 : 6]$ , prepared from the corresponding trinitro-compound by reduction with stannous chloride and hydrochloric acid, crystallises in white needles; its melting point could not be determined; it does not melt up to  $140^{\circ}$ , and suffers complete decomposition between  $140^{\circ}$  and  $150^{\circ}$ . The hydrochloride gives a greenish-brown coloration with sodium nitrite, and a reddish-black coloration with diazobenzene chloride.

By the nitration of 1 : 3 : 4 metaxylidene, the two nitrometaxylidines already mentioned, melting at  $78^{\circ}$  and  $123^{\circ}$  respectively, were obtained. By treatment with ethyl nitrite, &c., to eliminate the amido-group, the nitrometaxylidene of melting point  $123^{\circ}$  was converted into the nitrometaxylene  $[\text{Me} : \text{Me} : \text{NO}_2 = 1 : 3 : 4]$ , boiling at  $245.5^{\circ}$  under 744 mm. pressure, and of sp. gr. 1.135 at  $15^{\circ}$ , already described by Tawildaroff (*Zeit. f. Chem.*, 1870, 418), and Harmsen (*Abstr.*, 1881, 49); this by reduction with iron and acetic acid, gave the unsymmetrical metaxylidene described by Hofmann (this Journal, 1877, i, 92) and Schmitz (*Abstr.*, 1879, 156). 1 : 3 : 4 aceto-xylide forms white crystals and melts at  $128^{\circ}$ .

*Consecutive nitrometaxylene*,  $\text{C}_6\text{H}_3\text{Me}_2\text{NO}_2 [\text{Me} : \text{NO}_2 : \text{Me} = 1 : 2 : 3]$ , is prepared by the action of ethyl nitrite, &c., on the nitroxylidene melting at  $78^{\circ}$ . It boils at  $225^{\circ}$  under 774 mm. pressure, and has a sp. gr. of 1.112 at  $15^{\circ}$ . Reduced with iron and acetic acid, it gives the consecutive metaxylidene described by Schmitz. 1 : 3 : 2 aceto-xylide crystallises in white needles and melts at  $174^{\circ}$ . A. J. G.

**Action of Chlorine, Bromine, and Iodine on Sodium Paracresolate.** By C. SCHALL and C. DRALLE (*Ber.*, 17, 2528—2536).—*I. Action of Chlorine.*—When chlorine is passed through anhydrous sodium paracresolate suspended in carbon bisulphide, the principal

product is *monochloroparacresol*,  $C_6H_4MeCl.OH$ . This compound yields no sulphonic acid, whilst *paracresol* yields an ortho-sulphonic acid, so that the chlorine atom is probably in the ortho-position to the OH group. This was proved by treating it with phosphoric chloride, when a dichlorotoluene melting at  $200^\circ$  was formed, which on oxidation yielded orthodichlorobenzoic acid. Its constitution is therefore  $[OH : Cl : Me = 1 : 2 : 4]$ . When the sodium salt of this substance is treated with methyl iodide, it yields *monochloroparacresyl methyl ether*, a colourless, feebly refracting liquid which boils at  $213-215^\circ$ , and has a sp. gr. of  $1.1493$  at  $2.425^\circ$  compared with water at the same temperature. This anisoil when carefully oxidised with chromic acid yields *monochloranistic acid*,  $OMe.C_6H_3Cl.COOH$ , which crystallises in white silky scales melting at  $214-215^\circ$ . The barium salt crystallises with  $3\frac{1}{2}$  mols.  $H_2O$ : the silver salt forms sparingly soluble scales.

II. *Action of Bromine*.—This is similar to that of chlorine. *Monobromoparacresol* is a colourless liquid boiling at  $213-214^\circ$ ; its sp. gr. is  $1.5468$  at  $24.5^\circ$ . This compound is isomeric with that obtained by Vogt and Henninger (Abstr., 1882, 729) by the direct bromination of *paracresol*. *Monobromoparacresyl methyl ether* boils at  $225-227^\circ$ , and has a sp. gr. of  $1.4182$  at  $24.5^\circ$ . *Monobromanistic acid* crystallises in needles melting at  $213-214^\circ$ ; its barium salt forms small needles containing  $3\frac{1}{2}H_2O$ : the silver salt is a flocculent amorphous precipitate; the copper salt crystallises in green plates with  $2\frac{1}{2}$  mols.  $H_2O$ .

A small quantity of *dibromoparacresol* was also formed during the action of the bromine on sodium *paracresolate*. This substance forms prisms belonging to the asymmetric system, and isomorphous with those of dichloroparacresol. *Dibromoparacresyl benzoate* crystallises in snow-white needles melting at  $91-91.5^\circ$ . The dibromide was also converted into the anisoil, but all attempts to oxidise this proved futile.

III. *Action of Iodine*.—This was similar to that of chlorine and bromine. As the authors were not able to isolate the moniodoparacresol it was converted into the methyl ether. *Moniodoparacresyl methyl ether* boils at  $237-238^\circ$ . *Moniodoanistic acid* is identical with that already described by Griess (*Annalen*, 117, 54) and by Petzer (*Annalen*, 146, 302), and melts at  $234-235^\circ$ .

*Diiodoparacresol* forms white plates melting at  $61-61.5^\circ$ . *Diiodoparacresyl acetate* forms white plates melting at  $62-62.5^\circ$ . *Diiodoparacresyl benzoate* melts at  $129.5-130^\circ$ .  
L. T. T.

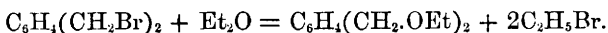
**Saponification of Haloid Ethers of the Benzene Series by Neutral Substances.** By A. COLSON (*Compt. rend.*, 99, 801-804).—The dibrominated derivatives of the three xylene glycols were heated with 2 mols.  $H_2O$  in sealed tubes at  $100^\circ$ , and the rate and limit of saponification were determined by estimating the amount of acid liberated. The maximum limit of saponification is reached more rapidly than in the case of the corresponding compounds in the methane series, and is the same for all three isomerides, and probably also for their homologues. The isomerides are, however, distinguished by the velocity of saponification, which is highest for the para- and lowest for the meta- derivative. In the case of the dibrominated

derivatives, the amount of acid liberated is only about 9 per cent. of the total acid, but as soon as this proportion is exceeded, the compounds rapidly decompose.

When the dibrominated derivatives are mixed with an equal weight of ordinary alcohol, and allowed to remain for several days at 30—32°, it is found that they are more rapidly attacked by the alcohol than the corresponding primary compounds in the methane series. The rate of saponification is highest for the meta- and lowest for the para-derivative, and this also holds good at 100°.

If the haloïd derivatives are heated with 2 molecular proportions of amyl alcohol in sealed tubes at 100°, it is found that the brominated derivatives decompose more rapidly than the chlorinated derivatives, whilst in each series decomposition ceases when about the same quantity of acid (about 5 per cent. of the total amount) has been liberated. The meta-derivative is almost completely decomposed, although only a small quantity of acid is set free. This result is explained by the formation of (?) bromamyline,  $\text{CH}_2\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{OC}_5\text{H}_{11}$ . It is evident that since the haloïd ethers are sensibly attacked by alcohol in the cold, and rapidly at 100°, this solvent should be avoided when working with these compounds.

The ethers of the methane series acting on these haloïd derivatives of the benzene series yield only one series of compounds, as shown in the equation—



C. H. B.

**Conversion of Phenols into Amines.** By K. BUCH (*Ber.*, 17, 2634—2641).—*Phenylparatolylamine* is formed from phenol and paratoluidine, and from paracresol and aniline, by heating them with an excess of zinc chloride at 260—300°; also in very small quantity by heating phenol and paratoluidine with calcium chloride at 300°. A better yield is obtained by the action of antimony trichloride on a mixture of aniline and paracresol at 260°, diphenylamine being, however, also produced. When paratoluidine and phenol are heated with phosphoric anhydride, ditolylamine is obtained, but no phenyltolylamine. *Paratoluidine* is produced on heating paracresol with ammonio-zinc chloride at or above 300°; ditolyl oxide,  $(\text{C}_7\text{H}_7)_2\text{O}$ , is also formed. This is moderately soluble in alcohol, and crystallises from it in silky scales, and from light petroleum in needles; it melts at 165° and volatilises at 100°. Ditolyl oxide is also formed when paracresol or a mixture of paracresol and paratoluidine is heated with zinc chloride. *Diphenylamine* is obtained in small quantity by the action of calcium chloride at 300° on aniline and phenol. It is also produced by the action of antimony trichloride on aniline, but a much better yield is obtained when a mixture of aniline and phenol is employed.

A. K. M.

**The Action of Cyanogen Chloride on Ortho- and Para-amidophenetoil.** By J. BERLINERBLAU (*J. pr. Chem.*, 30, 97—115).—By the action of cyanogen chloride on aniline, cyananilide and

diphenylguanidine are produced (Hofmann); its action on ortho- and para-amidophenetoil in ethereal solution is now studied and shown to be similar. *Orthoethoxyphenylcyanamide*,  $\text{EtO.C}_6\text{H}_4.\text{NHCN}$ , forms crystals melting at  $94^\circ$ , almost insoluble in water, and which do not polymerise on keeping or heating. If heated with hydrochloric acid at  $120^\circ$ , it does not yield orthoxyphenylcyanamide, but orthamidophenol; when treated in ethereal solution with dry hydrochloric acid, a syrup separates out unsuited for further examination. When treated with sodium alcoholate, the crystalline and stable sodium salt,  $\text{EtO.C}_6\text{H}_4.\text{NNaCN}$ , separates, which is reconverted into the original cyanamide by the action of acids: no polymerisation occurs. With silver nitrate, an aqueous solution of this salt gives a curdy precipitate of the *silver salt*,  $\text{EtO.C}_6\text{H}_4.\text{NAgCN}$ . The behaviour of these salts with ethyl iodide and also with iodine was partially studied. This and the following silver salt are readily decomposed by sulphuretted hydrogen, but no polymerisation takes place as with silver cyanamide.

*Paraethoxyphenylcyanamide* melts at  $78^\circ$ ; only its silver salt could be obtained. Once crystals melting at  $160^\circ$  were obtained, containing 1 mol.  $\text{H}_2\text{O}$  more; they are *paraethoxyphenylcarbamide*,  $\text{EtO.C}_6\text{H}_4.\text{NH.CONH}_2$ . This substance can also be prepared by mixing solutions of the hydrochloride of para-amidophenetoil with potassium cyanate; it is almost insoluble in water; it is not converted into the cyanamide or in any way altered by phosphoric anhydride. Treated for a long time with nitrous acid in alcoholic solution, a red precipitate,  $\text{C}_9\text{H}_{11}\text{N}_2\text{O}_2.\text{NO}_2$ , separates; if the acid acts for a short time only, an intermediate substance is formed insoluble in water, but decomposing very rapidly.

These substituted cyanamides can also be obtained from the corresponding thiocarbamides.

*Orthoethoxyphenylthiocarbamide*.—Orthamidophenetoil is evaporated with ammonium thiocyanate, and the residue washed with water. It melts at  $110^\circ$ . Mixed with lead hydroxide and dilute caustic soda, the lead sulphide filtered off, and acetic acid added, the above-described orthoethoxyphenylcyanamide separates.

*Paraethoxyphenylthiocarbamide* was likewise prepared and converted into the corresponding cyanamide. H. B.

**A Lakmoïd.** By M. C. TRAUB and C. HOCK (*Ber.*, 17, 2615—2617).—When a mixture of resorcinol (100 parts), sodium nitrite (5 parts), and water (5 parts), is gradually heated to  $110^\circ$ , a brisk reaction sets in and the mass assumes a red colour; when the reaction becomes less vigorous the heat may be raised to  $115$ — $120^\circ$ ; ammonia is then abundantly evolved whilst the melt becomes reddish-violet, bluish-violet, and finally blue. The product yields a blue solution with water, and on the addition of hydrochloric acid a precipitate is obtained; this, when dried, forms lustrous reddish-brown grains insoluble in chloroform and benzene, but readily soluble in alcohol, acetone, &c., less so in ether and pure water; these solutions have a red colour which resembles that of many red wines or raspberry-juice, and is changed to blue by the addition of a trace of alkali. This dye

also dissolves in boiling concentrated hydrochloric acid, yielding a bluish-green solution, and in concentrated sulphuric acid to a deep-blue solution. The absorption-spectrum of the alkaline solution resembles that of litmus, but the absorption-band is not so strong. It also resembles litmus in its behaviour on reduction, the alkaline solution being rapidly decolorised by hydrogen sulphide, but the colour is restored on exposure to the air. The authors hope to prove the identity of this artificial colouring matter with the chief constituent of litmus.

A. K. M.

**Substitution of the Amido-group in Aromatic Derivatives by Chlorine, Bromine, and Cyanogen.** By T. SANDMEYER (*Ber.*, 17, 2650—2653).—This is a continuation of experiments recently described (*Abstr.*, 1884, 1311). In order to convert metanitrilaniline into metachloronitrobenzene, 4 grams of the former together with 7 grams concentrated hydrochloric acid (sp. gr. 1.17), 100 grams water, and 20 grams of a 10 per cent. solution of cuprous chloride, are heated nearly to boiling and then a solution of 2.5 grams sodium nitrite in 20 grams water is added drop by drop. In the same way, parachlorotoluene has been obtained from paratoluidine, orthochlorotoluene from orthotoluidine, and orthochlorophenol from orthamidophenol, but in the case of the two ortho-derivatives the yield is small. Paraphenylenediamine and metaphenylenediamine also yield the corresponding dichlorobenzenes. To obtain bromobenzene from aniline, 12.5 grams copper sulphate, 36 grams potassium bromide, 80 grams water, 11 grams sulphuric acid (sp. gr. 1.8), and 20 grams copper turnings are boiled together until the solution is nearly decolorised, 9.3 grams aniline added, the whole again heated nearly to boiling, and then a solution of 7 grams sodium nitrite in 40 grams water gradually dropped in. The product is distilled, washed with soda and water, extracted with ether, dried, and fractioned. The amido-group may also be replaced by cyanogen: 28 grams of a 96 per cent. solution of potassium cyanide are added to a hot solution of 25 grams copper sulphate in 150 grams water, the solution heated to about 90°, and a solution of diazobenzene chloride gradually introduced. The whole is then distilled, the oil extracted with ether, washed with soda solution and with dilute sulphuric acid, and then fractioned. The amount of benzonitrile boiling at 184° obtained is 63 per cent. of the theoretical amount.

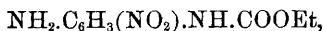
A. K. M.

**Action of Ethyl Chlorocarbonate on Paranitrilaniline.** By H. HAGER (*Ber.*, 17, 2625—2632).—*Paranitrophenylurethane* (*phenylene-paranitrourethane*),  $\text{NO}_2\text{C}_6\text{H}_4\text{NH.COOEt}$ , is prepared by heating paranitrilaniline (6 grams) with ethyl chlorocarbonate (6 grams) for about three hours at 120—130°. It is sparingly soluble in water, readily in alcohol, from which it crystallises in long, brown, silky needles melting at 129°. The mother-liquors contain a very small quantity of a crystalline compound of metallic lustre which imparts a blue colour to silk. *Paramidophenylurethane*, obtained by reducing the nitro-compound, is sparingly soluble in water, readily in benzene, from which it crystallises in long, brown, transparent prisms melting at 71—72°; with ferric chloride, it yields a green precipitate which

at once turns black and is readily soluble in alcohol with violet coloration. It does not yield a carbamide when heated. The hydrochloride,  $C_9H_{12}N_2O_2.HCl$ , forms readily soluble colourless needles; the mercury compound,  $(C_9H_{12}N_2O_2.HCl)_4.HgCl_2$ , crystallises from a hydrochloric acid solution in long violet needles; the stannichloride,  $(C_9H_{12}N_2O_2.HCl)_3.SnCl_4$ , forms colourless scales; the platinumchloride,  $(C_9H_{12}N_2O_2)_2.H_2PtCl_6$ , is a light brown precipitate, and is decomposed by boiling with water; the sulphate,  $C_9H_{12}N_2O_2.SO_4H_2$ , is readily soluble and crystallises in concentrically grouped arborescent forms; the oxalate,  $C_9H_{12}N_2O_2.C_2O_4H_2$ , crystallises in violet needles, very sparingly soluble in cold, readily in hot water. *Parabenzoylamidophenylurethane* (*phenyleneparamidobenzoylurethane*),



is obtained on gradually adding a mixture of benzene and benzoic chloride to a cold solution of phenyleneparamidourethane in benzene. It is insoluble in water, sparingly soluble in alcohol, from which it crystallises in slender violet needles melting at  $230^\circ$ ; by the action of nitric acid (sp. gr. 1.530), a small quantity of a trinitro-derivative is obtained; this melts at  $210^\circ$  and crystallises from alcohol in slender yellow needles. When paramidophenylurethane hydrochloride and benzoic chloride, in molecular proportions, are heated together at  $140$ — $150^\circ$ , a substance is obtained which appears to have the formula  $N(C_6H_4.NHBz)_2.CO\bar{O}Et$ . It is insoluble in water, very sparingly soluble in alcohol and glacial acetic acid, and crystallises in slender colourless needles melting above  $360^\circ$ . *Orthoparadinitrophenylurethane*,  $C_6H_3(NO_2)_2.NH.CO\bar{O}Et$ , is obtained by the nitration of paranitrophenylurethane in the cold. It melts at  $110$ — $111^\circ$ , dissolves sparingly in hot water, more readily in alcohol, from which it crystallises in light brown needles. When its alcoholic solution is warmed with potassium hydroxide, ammonia is given off and *diorthoparadinitrophenylamine* (*tetranitrodiphenylamine*),  $NH(C_6H_3N_2O_4)_2$ , is produced; this melts at  $180^\circ$ , is sparingly soluble in alcohol, more readily in glacial acetic acid, crystallises from the former in reddish-brown scales, and from the latter in yellow needles and prisms; with caustic alkali, it yields a dark red solution, which gives off ammonia when heated. When orthoparadinitrophenylurethane is submitted to the action of ammonium sulphide, *orthamidoparanitrophenylurethane*,



is produced. This is very sparingly soluble in water, readily in alcohol, and crystallises in orange-red needles or prisms melting at  $162^\circ$ ; it is decomposed by dilute acids into alcohol and the carbamide-derivative,  $NO_2.C_6H_3<\begin{smallmatrix} NH \\ NH \end{smallmatrix}>CO$ . This is sparingly soluble in water, readily in alcohol, from which it crystallises in colourless needles which do not melt at  $300^\circ$ ; it is also readily soluble in cold alkali. By the action of tin and hydrochloric acid on orthoparadinitrophenylurethane, both nitro-groups are reduced, alcohol is eliminated, and the carbamide-derivative,  $C_6H_3(NH_2.HCl)<\begin{smallmatrix} NH \\ NH \end{smallmatrix}>CO.HCl$ , is obtained. This

is extremely soluble in water, less so in hydrochloric acid, from which it crystallises in nodular groups of small violet needles. The zinc double salt,  $C_7H_7N_3O, 2HCl, ZnCl_2$ , crystallises from hydrochloric acid in long, dense, graphite-like needles of metallic lustre. The platinic and mercuric double salts decompose very readily. The picrate,  $C_7H_7N_3O, C_6H_3N_3O_7$ , forms greenish-yellow needles. A. K. M.

**Oxidation of Paratoluidine.** By H. KLINGER and R. PITSCHKE (*Ber.*, 17, 2439—2444).—The oxidation of paratoluidine has been investigated by Barsilowsky (*Abstr.*, 1879, 237) who used an alkaline solution of potassium ferricyanide, and by Perkin (*Trans.*, 1880, 546), using chromic acid. The same substance, of the empirical formula  $C_7H_7N$ , was obtained by both observers, but was regarded by Barsilowsky as a polymerised azotoluene, whilst Perkin considered that it was probably a triparatolylenetriamine,  $(C_7H_6)_3N_3H_3$ ; the authors have therefore re-examined the compound. The substance was prepared by oxidation of paratoluidine with an alkaline ferricyanide solution, and its identity with that obtained by the other authors determined by crystallographic measurement. It melts at  $220\text{--}225^\circ$  ( $216\text{--}220^\circ$ , Perkin;  $244\text{--}245^\circ$ , Barsilowsky). Its salts can be obtained by shaking a solution of the base in benzene with dilute aqueous acids, as dark violet or iridescent crystalline precipitates; they are partly decomposed by washing and drying. The *hydrochloride*,  $C_{26}H_{28}N_4, 2HCl$ , was obtained in a pure state, and then forms lustrous, violet plates, readily soluble in water and alcohol with intense reddish-violet coloration; on addition of alkalis, the base is liberated. By the action of stannous chloride followed by tin and hydrochloric acid on a solution of the base in alcohol and hydrochloric acid, it is converted into paratoluidine and a leuco-base,  $C_{21}H_{33}N_3$ . As paratoluidine is also formed by the action of hydrochloric acid on the base, it appears most probable that the latter is an amido-azo-compound of the formula  $\dot{C}_{21}H_{17}(NH_2).N_2.C_7H_7$ .

*Paraleucotoluidine*,  $C_{21}H_{23}N_3$ , crystallises in thin, white plates, which very soon turn red; it melts at  $150^\circ$ , is very readily soluble in cold alcohol or in hot water or hot aqueous soda. The *hydrochloride*,  $C_{21}H_{23}N_3, 3HCl + H_2O$ , forms colourless prisms or slender needles.

*Pararosatoluidine* is prepared by oxidation of the leuco-base by a current of air, or more conveniently from the hydrochloride by the action of a strongly alkaline ferricyanide solution. It crystallises in reddish-brown plates having a green lustre, melts at  $150^\circ$ , and is decomposed at higher temperatures with formation of ammonia and toluidine. It is readily soluble in alcohol, ether, and benzene, and dissolves in concentrated sulphuric acid with purple-red colour. A. J. G.

**Two Isomeric Isobutylorthamidotoluenes.** By J. EFFRONT (*Ber.*, 17, 2317—2351).—The author has already shown that an isobutylorthamidotoluene is obtained by heating orthotoluidine hydrochloride with isobutyl alcohol at  $300^\circ$  differing from that prepared by Erhardt (*Inaug. Diss.*, Zurich, 1882) by heating isobutyl alcohol and orthotoluidine with zinc chloride. This latter substance



has the constitution  $[\text{Me} : \text{Bu}^\beta : \text{NH}_2 = 1 : 3 : 2]$ , whilst the base obtained by the author is expressed by  $[\text{Me} : \text{Bu}^\beta : \text{NH}_2 = 1 : 5 : 2]$ .

5.2 ISOBUTYLORTHAMIDOTOLUENE,  $\text{C}_6\text{H}_3\text{MeBu}^\beta.\text{NH}_2$   $[1 : 5 : 2]$ , obtained as above mentioned, forms a nearly colourless liquid of agreeable aromatic odour, which turns yellow on exposure to light, does not solidify in a mixture of ice and salt, boils at  $243^\circ$ , and readily distils with steam. It is nearly insoluble in water, but mixes in every proportion with alcohol and ether, and forms well characterised salts. The *hydrochloride*,  $\text{C}_{11}\text{H}_{17}\text{N}.\text{HCl}$ , crystallises in long, thin needles. It is sparingly soluble in cold, readily soluble in hot water. By long boiling of its aqueous solution, the salt suffers dissociation. The *hydrobromide*,  $\text{C}_{11}\text{H}_{17}\text{N}.\text{HBr}$ , crystallises in long needles. The *sulphate*,  $(\text{C}_{11}\text{H}_{17}\text{N})_2.\text{H}_2\text{SO}_4$ , crystallises in white needles, sparingly soluble in cold water. The *oxalate*,  $(\text{C}_{11}\text{H}_{17}\text{N})_2.\text{H}_2\text{C}_2\text{O}_4$ , crystallises in silvery needles readily soluble in hot water, alcohol, and ether. The *acetyl-derivative*,  $\text{C}_6\text{H}_3\text{MeBu}^\beta.\text{NHAc}$ , crystallises in greyish-white plates, melts at  $162^\circ$ , is sparingly soluble in hot water, readily soluble in alcohol. The *benzoyl-derivative*,  $\text{C}_6\text{H}_3\text{MeBu}^\beta.\text{NHBz}$ , forms small white needles, melts at  $168^\circ$ , and is sparingly soluble in hot water or cold alcohol.

*Isobutylorthocresol*,  $\text{C}_6\text{H}_3\text{MeBu}^\beta.\text{OH}$   $[1 : 5 : 2]$ , prepared by means of the diazo reaction from the amine, is a thick, pale-yellow liquid of faint aromatic odour, sparingly soluble in water, readily soluble in alcohol, ether, and dilute aqueous soda.

*Isobutylorthiodotoluene*,  $\text{C}_6\text{H}_3\text{MeBu}^\beta\text{I}$   $[1 : 5 : 2]$ , prepared by the action of hydriodic acid on the crude solution of the diazo-chloride, forms long white needles, melts at  $34-35^\circ$ , and boils at  $264-265^\circ$ . By oxidation with chromic acid, it is completely oxidised; by heating with dilute nitric acid, it is oxidised to nitrotolylisobutyric acid, or by further action it is converted into nitrotolylpropionic acid.

*Nitrotolylisobutyric acid*,



crystallises in white needles, melts at  $139^\circ$ , can be sublimed, is sparingly soluble in cold, readily soluble in boiling water, sparingly soluble in light petroleum, readily soluble in alcohol and ether. The *silver salt*,  $\text{C}_6\text{H}_{12}(\text{NO}_2).\text{COOAg}$ , crystallises in colourless plates, and is readily soluble in hot water.

*Nitrotolylpropionic acid*,  $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2).\text{CH}_2.\text{CH}_2.\text{COOH}$ , crystallises in thick white needles, melts between  $130-136^\circ$ , and is less soluble in boiling water than the preceding acid.

Experiments to convert isobutylorthamidotoluene into the hydrocarbon by the action of ethyl nitrite were not successful. It was therefore converted into the azo-chloride, and this treated with stannous chloride, when a hydrocarbon was obtained agreeing in all particulars with Kelbe's metaisobutyltoluene (Abstr., 1881, 809).

*Tolylpropionic acid*,  $\text{C}_6\text{H}_4\text{Me}.\text{CH}_2.\text{CH}_2.\text{COOH}$   $[\text{Me} : \text{C}_3\text{H}_5\text{O}_2 = 1 : 3]$ , is obtained by heating metaisobutyltoluene with excess of nitric acid (sp. gr. 1.15) for five hours at  $180^\circ$ , it crystallises in white needles, melts at  $125^\circ$ , and sublimes readily. It is scarcely soluble in cold, sparingly soluble in hot water, readily soluble in alcohol and ether.

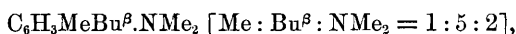
The *silver* salt,  $C_9H_{11}.COOAg$ , is crystalline, sparingly soluble in cold, readily soluble in hot water. On oxidation, the acid is converted into isophthalic acid.

*Isobutylorthoformotoluide*,  $C_6H_3MeBu^{\beta}.NH.CHO$  [1 : 5 : 2], is obtained by heating isobutylorthamidotoluene with formic acid at  $250^{\circ}$ ; it crystallises in colourless tables, melts at  $105-106^{\circ}$ , is sparingly soluble in hot water, readily soluble in alcohol and ether. If heated with excess of zinc-dust, it is converted into *isobutylorthotolunitrile*,  $C_6H_3MeBu^{\beta}.CN$ . This crystallises in long, white needles, melts at  $59-60^{\circ}$ , boils at  $248-249^{\circ}$ , is readily soluble in alcohol and ether, sparingly soluble in light petroleum, and insoluble in water. *Isobutyl-orthotoluic acid*,  $C_6H_3MeBu^{\beta}.COOH$  [1 : 5 : 2], is obtained, although with difficulty, by the action of alcoholic potash on the nitrile; it crystallises in white needles, melts at  $140^{\circ}$ , is sparingly soluble in hot water, readily soluble in alcohol and ether. The *silver* salt forms colourless plates of the formula  $C_{11}H_{15}.COOAg$ . By oxidation with dilute nitric acid at  $240^{\circ}$ , it is converted into trimellitic acid, thus showing the parent isobutylorthamidotoluene to have the constitution



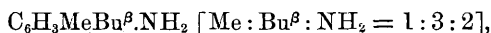
*Di-orthotoluisobutylthiocarbamide*,  $CS(NH.C_6H_3MeBu^{\beta})_2$ , prepared by heating an alcoholic solution of isobutylorthamidotoluene with excess of carbon bisulphide, crystallises in long, thin, silky needles; melts at  $184^{\circ}$ ; is sparingly soluble in hot alcohol, readily soluble in ether. *Orthotoluisobutylthiocarbimide*,  $C_6H_3MeBu^{\beta}.NCS$ , is obtained in small quantity in the preparation of the thiocarbamide, but is best prepared by heating the thiocarbamide with syrupy phosphoric acid. It forms long needles, melts at  $46^{\circ}$ , boils, with partial decomposition, at  $275-280^{\circ}$ , and is sparingly soluble in light petroleum, readily soluble in alcohol and ether. When heated with metallic copper, it yields isobutylorthotolunitrile.

*Dimethylorthotoluisobutylamine*,



prepared by heating isobutylorthamidotoluene with methyl iodide and decomposing the resulting ammonium iodide by digestion with silver oxide, forms an oil of aromatic odour, boiling at  $250-251^{\circ}$ . The *hydrochloride* is white and crystalline. The *platinochloride*,  $(NMe_2C_{11}H_{15})_2.H_2PtCl_6$ , forms a red crystalline mass.

### 3. 2 ISOBUTYLORTHAMIDOTOLUENE,



was prepared according to Erhardt's method (*loc. cit.*); his description of the properties and derivatives of the base is confirmed by the author. Converted into the diazo-chloride, and treated with zinc chloride, it also yields metaisobutyltoluene. As according to theory only two isobutylorthamidotoluenes can be derived from metaisobutyltoluene, and as the constitution 1 : 5 : 2 has been shown to belong to the author's base, it follows that Erhardt's base must be the 1 : 3 : 2 compound. The following derivatives were prepared by methods similar to those employed for the corresponding derivatives of the 1 : 5 : 2

base. *Isobutylorthoformotoluide*,  $C_6H_3MeBu^{\beta}.NH.CHO$  [= 1 : 3 : 2], crystallises in white tables, melts at  $103-105^{\circ}$ , is nearly insoluble in water, readily soluble in ether and alcohol. *Isobutylorthotolunitrile*,  $C_6H_3MeBu^{\beta}.CN$  [1 : 3 : 2], is a colourless oil, can be solidified in a freezing mixture, boils at  $242-244^{\circ}$ , and is readily soluble in alcohol and ether. *Isobutylorthotoluic acid*,  $C_6H_3MeBu^{\beta}.COOH$  [1 : 3 : 2], crystallises in silvery plates, melts at  $132^{\circ}$ , is sparingly soluble in hot water, readily soluble in ether and alcohol. The silver salt,  $C_{11}H_{15}.COOAg$ , crystallises in colourless plates. *Di-orthotoluisobutylthiocarbamide*,  $CS(NH.C_6H_3MeBu^{\beta})_2$ , crystallises in white needles, melts at  $175^{\circ}$ , and is soluble in hot alcohol. *Orthotoluisobutylthiocarbimide*,  $C_6H_3MeBu^{\beta}NCS$ , forms a white crystalline mass, melts at  $44^{\circ}$ , and boils at  $267^{\circ}$ . It was further converted into the corresponding nitrile and 1, 3, 2 isobutylorthotoluic acid. A. J. G.

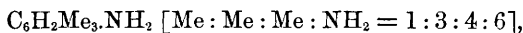
**Derivatives of Benzoylpseudocumidine: Constitution of Pseudocumidine and Benzaniline.** By E. FROEHLICH (*Ber.*, 17, 2673—2681).—In a previous paper (*Abstr.*, 1884, 1319), the author mentioned the formation of *benzoylphthalopseudocumidic acid*,



as an intermediate product of the action of alcoholic potash on benzoylphthalopseudocumide. It is insoluble in water, and crystallises from alcohol in colourless microscopic needles melting at  $195^{\circ}$  with separation of water; the substance, dried in a vacuum, contains 1 mol.  $H_2O$ . The *acetyl-derivative of benzoylpseudocumidine*,

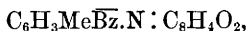


is insoluble in water, sparingly soluble in alcohol, ether, and cold glacial acetic acid, and crystallises from the hot acid in large, colourless, lustrous needles, melting at  $170^{\circ}$ . Attempts to prepare the isocyanide of benzoylcumidine were unsuccessful, whilst the carbamide and thiocarbamide could not be obtained in a crystalline form, but only as resins. The *urethane*,  $C_6HMe_3\bar{Bz}.NH.COOEt$ , crystallises from dilute alcohol in slender, colourless, silky needles melting at  $105^{\circ}$ . *Dimethylbenzoylpseudocumidine methiodide*,  $C_6HMe_3\bar{Bz}.NMe_2.MeI$ , crystallises in magnificent, broad, colourless prisms which, when placed in a vacuum, lose water and fall to a powder; the substance then melts at  $187^{\circ}$  with decomposition. The author discusses the constitution of pseudocumidine, and shows that its formula is



the amido-group occupying the same position as the hydroxyl-group in pseudocumenol. It is evident from this formula that the benzoyl-group in benzoylpseudocumidine cannot occupy the para-position to the amido-group, and from the close relationship between benzoylpseudocumidine and benzoylaniline, it is also improbable that this latter substance is a para-derivative, as assumed by Doebner (*Annalen*, 210, 266). The author thinks that it is more probably orthamido-benzophenone. Of the phthalic derivatives of the three toluidines, that from paratoluidine alone gives a crystalline benzoyl-compound,

whilst the other two yield resinous products. *Phthalorthotoluide*,  $C_6H_4Me.N:C_6H_4O_2$ , obtained by heating together orthotoluidine and phthalic anhydride, is insoluble in water, sparingly soluble in alcohol and ether, readily in hot glacial acetic acid, from which it crystallises in colourless needles melting at  $182^\circ$ ; it is converted into phthalorthotoluidic acid when heated with alcoholic potash or ammonia. *Phthalometatoluide* is insoluble in water, dissolves sparingly in alcohol and ether, readily in hot glacial acetic acid, and forms small colourless needles melting at  $153^\circ$ ; it yields phthalometatoluidic acid when treated with alcoholic potash or ammonia. *Phthaloparatoluide* melts at  $204^\circ$  (according to Michael at  $200^\circ$ , *Ber.*, **10**, 579), and is converted by alcoholic ammonia or potash into phthaloparatoluidic acid. When phthaloparatoluide (75 grams) and benzoic chloride (45 grams) are heated at  $170$ – $180^\circ$  for 6 to 8 hours with a little zinc chloride, hydrochloric acid is evolved, and *benzoylphthaloparatoluide*,



is obtained, accompanied, however, by a second substance not yet isolated. Benzoylphthaloparatoluide melts at  $202^\circ$ , is insoluble in water, sparingly soluble in alcohol and ether, and readily in hot glacial acetic acid, from which it separates in dense, well-formed, tetragonal crystals. When heated with alcoholic potash, it is converted first into benzoylphthaloparatoluidic acid, and then into a yellow-coloured base. It also yields a yellow base (probably benzoyltoluidine) with concentrated sulphuric acid. The second substance mentioned above appears to be an isomeric compound,  $C_{22}H_{15}NO_3$ , of lower melting point; it also yields a yellow base when treated with concentrated sulphuric acid.

A. K. M.

**Derivatives of Parahydroxydiphenylamine.** By M. PHILIP and A. CALM (*Ber.*, **17**, 2431–2438).—A continuation of Calm's researches on this subject (*Abstr.*, 1884, 592). *Parahydroxydiphenylamine hydrobromide*,  $C_{12}H_{11}NO.HBr$ , prepared by the action of hydrobromic acid on a solution of the base in anhydrous benzene, crystallises in pale rose-coloured needles, and is very unstable.

*Nitrosoparahydroxyphenylamine*,  $OH.C_6H_4.NPh.NO$ , is prepared by adding sodium nitrite to a well-cooled solution of the base in hydrochloric acid. It forms yellow crystalline plates, or needles, or red tables, melts at  $95^\circ$ , and is readily soluble in benzene, alcohol, ether, glacial acetic acid, and light petroleum. It behaves as a nitrosamine, giving Liebermann's reaction.

*Methylparamethoxydiphenylamine*,  $OMe.C_6H_4.NMePh$ , is prepared by heating parahydroxydiphenylamine (1 mol.) with methyl iodide (2 mols.), potash (2 mols.), and a little methyl alcohol for two hours at  $120$ – $130^\circ$ . It forms a pale yellow oil of violet-like odour, and boils at  $313^\circ$ . It rapidly turns brown on exposure to air. It behaves like a tertiary amine, and yields a green colouring matter when heated with zinc chloride and benzotrichloride.

*Ethylparaethoxydiphenylamine*,  $OEt.C_6H_4.NPhEt$ , resembles the methyl-compound, and boils at  $318$ – $320^\circ$ .

*Para-isobutoxydiphenylamine*,  $OBu^i.C_6H_4.NHPh$ . Although prepared

in a manner similar to the compounds just described, only the hydroxylic hydrogen is replaced by isobutyl in this compound. It forms pale yellow quadratic plates, melts at  $68^{\circ}$ , and is readily soluble in benzene, alcohol, ether, and light petroleum.

*Formylparahydroxydiphenylamine*,  $\text{OH.C}_6\text{H}_4.\text{NPh.CO.H}$ , prepared by heating the base with sodium formate and excess of formic acid, crystallises in white needles, melts at  $178^{\circ}$ , is soluble in ether, hot benzene, and glacial acetic acid, readily soluble in hot alcohol.

*Diacetylparaoxydiphenylamine*,  $\text{OAc.C}_6\text{H}_4.\text{NPhAc}$ , prepared in a similar manner to the formyl-compound, forms large colourless prisms terminated by pyramids, apparently of the rhombic system, melts at  $120^{\circ}$ , and is readily soluble in hot benzene, alcohol, ether, and glacial acetic acid.

*Dibenzoylparaoxydiphenylamine*,  $\text{OBz.C}_6\text{H}_4.\text{NPhBz}$ , prepared by heating the base with benzoic chloride, forms pale yellow, compact, prismatic crystals, melts at  $175^{\circ}$ , is sparingly soluble in cold, soluble in hot alcohol, more readily soluble in glacial acetic acid, benzene, and ether. On nitration, it is converted into a *dinitro*-compound,  $\text{C}_{26}\text{H}_{17}\text{NO}_3(\text{NO}_2)_2$ , forming a pale yellow, crystalline mass, which melts at  $194\text{--}195^{\circ}$ , is readily soluble in hot glacial acetic acid, moderately soluble in ether and hot benzene, very sparingly soluble in alcohol. It gives a red coloration with concentrated aqueous soda or potash; addition of hydrochloric acid to the alkaline solution causes the formation of a reddish-brown flocculent precipitate.

A. J. G.

#### Action of Carbon Bisulphide on Metaphenylenediamine.

By P. GUCCI (*Ber.*, 17, 2656—2658).—When an alcoholic solution of metaphenylenediamine is heated with carbon bisulphide, the solution becomes red, and hydrogen sulphide is abundantly evolved; this continues for about eight hours, and as it ceases thin, red prismatic crystals make their appearance. These are insoluble in water, alcohol, ether, carbon bisulphide and benzene, but dissolve very readily in ammonia, with orange-yellow coloration, and separate out again on heating the solution to  $50\text{--}60^{\circ}$ . From the results obtained on analysis, this substance appears to be a *thiocarbonylphenylenediaminethiocarbonate*,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} > \text{SC.S}_2\text{C}$ . When the mother-liquor from these crystals is warmed, hydrogen sulphide is again evolved, and a yellow amorphous substance gradually separates, which is insoluble in water, alcohol, ether, carbon bisulphide, benzene, and cold ammonia. Its formula appears to be  $\text{C}_{20}\text{H}_{20}\text{N}_6\text{S}_2$ , so that it may be derived either from 1 mol.  $\text{C}_6\text{H}_4(\text{N}:\text{CS})_2$  and 2 mols. phenylenediamine, or from 3 mols. phenylenediamine and 2 mols. carbon bisulphide, in which latter case it would be a *dithiocarbonyltriphenylenediamine*,  $\text{NH}_2.\text{C}_6\text{H}_4.\text{NH}.\text{SC}.\text{NH}.\text{C}_6\text{H}_4.\text{NH}.\text{SC}.\text{NH}.\text{C}_6\text{H}_4.\text{NH}_2$ . On pouring the mother-liquor from this into water, a third substance,  $\text{C}_{12}\text{H}_{12}\text{N}_3\text{S}_2$ , is obtained as an abundant orange-yellow amorphous precipitate, extremely soluble in alcohol.

A. K. M.

**Mixed Azo-compounds.** By E. BAMBERGER (*Ber.*, 17, 2415—2422).—*Ethyl orthonitrophenylazoacetoacetate*,



is prepared by dissolving 3 grams orthonitraniline in hydrochloric acid, cooling with a mixture of ice and salt, and adding a dilute aqueous solution of 1.5 grams of sodium nitrite; after remaining for 12 hours, the mixture is largely diluted with water, neutralised with soda, and a dilute solution of ethyl acetoacetate (2.9 grams) and potash (1.3 grams) added drop by drop. After adding a few drops of soda, the mixture is allowed to remain for a day in a warm place, when the new product separates as a hard crystalline crust. It is obtained on recrystallisation in lustrous golden-yellow plates, melts at 92—93°, is readily soluble in alcohol, ether, glacial acetic acid, and chloroform, and also soluble in hot water.

*Orthonitrophenylazoacetic acid*,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{N}_2.\text{CHAc}.\text{COOH}$ , is prepared by heating the ethyl salt on the water-bath with potash for 1—2 minutes, the potash salt which separates then being decomposed by hydrochloric acid. It crystallises in lustrous golden-brown plates resembling mosaic gold; when heated, it blackens at 183° and melts at 185° with evolution of carbonic anhydride; it is readily soluble in glacial acetic acid, glycerol, and hot alcohol, sparingly soluble in ether and cold alcohol. The *ammonium* salt forms golden-yellow needles, the *lead* salt a yellow powder, the *copper* salt is obtained in green flocks, and the *barium* salt crystallises in tufts of yellow needles.

*Orthonitrophenylazoacetone*,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{N}_2.\text{CH}_2.\text{COMe}$ , is obtained by heating the acid (best mixed with glycerol), by heating either the free acid or the ethyl salt with potash or, best, as follows: an alcoholic solution of orthonitraniline is treated with the nitrogen oxides evolved by the action of nitric acid on arsenious anhydride, the product of the reaction is poured into water, filtered, and the filtrate mixed with ethyl acetoacetate and potash, and the whole digested for 15 minutes at 40°. The mixture of nitrophenylazoacetone and a little ethylic nitrophenylazoacetoacetate which is then precipitated, is heated for a few minutes with alcoholic potash and poured into a large volume of water, when the ketone separates in voluminous yellow flocks and can be purified by crystallisation. It crystallises in long, silky, sulphur-yellow needles, melts at 123—124°, and is soluble in all the ordinary solvents, but is insoluble in alkalis.

*Orthoamidazoacetic acid*,  $\text{C}_6\text{H}_4(\text{NH}_2).\text{N}_2.\text{CHAc}.\text{COOH}$ , obtained by the reduction of the nitro-acid with ferrous sulphate and ammonia, crystallises in satiny orange-red tables, melts with decomposition at 157°, is very readily soluble in glacial acetic acid and chloroform, moderately soluble in ether, somewhat soluble in water. It is very unstable.

The corresponding members of the toluidine series were prepared by similar methods from metanitroparatoluidine.

*Metanitrotolylparazoacetic acid*,  $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2).\text{N}_2.\text{CHAc}.\text{COOH}$ , crystallises in long yellow needles, melts at 176°, is readily soluble in glacial acetic acid, alcohol, and glycerol. It is converted into the corresponding ketone by the action of heat or of alkalis.

*Metanitrotolylparaazoacetone*,  $C_6H_3Me(NO_2).N_2.CH_2.COME$ , crystallises in lustrous orange-red prisms and melts at  $134-134.5^\circ$ .

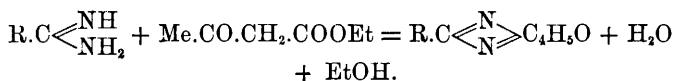
*Metamidoparaazoacetoacetic acid*,  $C_6H_3Me(NH_2).N_2.CH\bar{A}c.COOH$ , forms brick-red needles and melts at  $162^\circ$ . A. J. G.

**Action of Acetic Anhydride on Benzamidine.** By A. PINNER (*Ber.*, 17, 2511—2516).—The author has reinvestigated the body  $C_{14}H_{13}N_3$ , described by himself and Klein (*Abstr.*, 1878, 491; 1883, 1099; and 1884, 1324) in order to determine whether this or  $C_9H_8N_2$  is its true formula. If its composition were  $C_9H_8N_2$ , it must have the constitution  $C_6H_5.C \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} CMe$ , and should then yield a carboxylic acid on oxidation; but neither permanganate nor chromic acid has any action on it. When bromine is added to a solution of the substance in chloroform, deep yellow needles are deposited which appear to be a bromine additive product. This compound is, however, very unstable, and the analytical results obtained agree as well for  $C_9H_8N_2.Br_2$  as for  $C_{14}H_{13}N_3.Br_3$ . When dissolved in fuming nitric acid, the original substance yields a compound which gives numbers corresponding fairly well with the formula  $C_{14}H_9(NO_2)_4N_3$ . The most conclusive proof of the correctness of the formula  $C_{14}H_{13}N_3$ , however, is the formation of a *monosulphonic acid*,  $C_{14}H_{12}N_3.SO_3H$ , by dissolving the original substance in fuming sulphuric acid. This acid crystallises in nodules with  $\frac{1}{2}H_2O$ , and loses its water of crystallisation at  $140^\circ$ , but is then partially decomposed. It forms a crystalline *sodium salt* soluble in water; the *barium salt* crystallises with  $10H_2O$  in glistening scales, very sparingly soluble in water. When fused with potash, the acid yields *parahydroxybenzoic acid*. When heated at  $100^\circ$  with concentrated hydrochloric acid, the original substance deposits a compound in shining scales, which is decomposed on the addition of water into the previously described hydrochloride. When heated with twenty times its weight of hydrochloric acid in closed tubes at  $100^\circ$ , the original substance is decomposed into benzoic acid and ammonium chloride.

From these results, there can be no doubt that the substance is *dibenzimidine*,  $NH : CPh.N : CPh.NH_2$ .

The author also attempted to determine the molecular weight of cyanphenine by preparing its sulphonic acid. The acid obtained contained one  $SO_3H$ -group to every seven carbon-atoms, and thus gave no clue to the molecular weight. L. T. T.

**Action of Ethyl Acetoacetate on the Amidines.** By A. PINNER (*Ber.*, 17, 2519—2520).—Ethyl acetoacetate reacts extremely readily with the amidines, water and alcohol being eliminated.

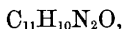


The compounds formed have basic properties and their constitution is

probably  $R.C \begin{smallmatrix} \text{N.CO—} \\ \text{N: CMe} \end{smallmatrix} > CH_2$ . By means of phosphoric chloride, &c., they may be converted into derivatives of the nucleus,



Benzamidine and ethyl acetoacetate thus yield a compound,



which crystallises in prisms melting at  $215.5-216^\circ$ , and is sparingly soluble in ether. It dissolves easily in acids, and yields a sparingly soluble platinochloride,  $(C_{11}H_{10}N_2O)_2, H_2PtCl_6 + H_2O$ . When heated with phosphoric chloride, the compound  $C_{11}H_{10}N_2O$  yields a substance of the formula  $C_{11}H_8N_2Cl$ , melting at  $71^\circ$ . This body is soluble in ether, insoluble in water, and crystallises in rhombic plates. The constitution of the chloride is probably  $CPh \begin{smallmatrix} \text{N.CCl—} \\ \text{N: CMe} \end{smallmatrix} > CH$ .

Acetamidine when similarly treated yields a compound,  $C_6H_8N_2O$ , which forms long silky needles soluble in water, sparingly so in ether.

The amidines also react easily with the cyanates and isothiocyanates. The author is now investigating these reactions.

L. T. T.

**So-called Phthalylacetamide.** By W. ROSER (*Ber.*, 17, 2623—2625).—This compound is an acid, and therefore cannot have the constitution implied by the name which was given to it by Gabriel. The author suggests the name *phthalimidylacetic acid*. The *calcium salt* contains  $\frac{1}{2}$  mol.  $H_2O$ , and forms a white crystalline precipitate, almost insoluble in water; the *barium salt* is readily soluble in hot water and crystallises in small prisms containing 2 mols.  $H_2O$ ; the *silver salt*,  $C_{10}H_6O_3NaAg$ , is insoluble and amorphous. When phthalimidylacetic acid is boiled with alkalis, ammonia is liberated and acetophenone-carboxylic acid produced. Of the two formulæ for phthalimidylacetic acid,  $CO \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{—N} \end{smallmatrix} > C.CH_2.COOH$ , and  $CO \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NH} \end{smallmatrix} > C:CH.COOH$ , the first is considered the more probable, for if the second formula were correct, the compound  $CO \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NMe} \end{smallmatrix} > C:CH.COOH$  should be formed by the action of methylamine on phthalylacetic acid; this, however, is not the case.

Gabriel's phthalylpropionamide is probably phthalimidylpropionic acid.

By the action of sodium-amalgam on phthalimidylacetic acid in alkaline solution, a dark violet-coloured liquid is obtained which yields an almost black precipitate on the addition of hydrochloric acid.

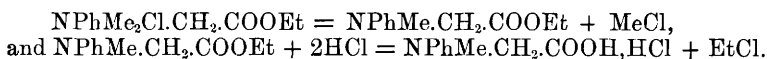
A. K. M.

**Preparation of Anthranilic Acid.** By H. KOLBE (*J. pr. Chem.*, 30, 124—125).—A former communication (this vol., p. 58) contains an account of the preparation of *isatoic acid* from isatin; this acid when boiled with concentrated hydrochloric acid is resolved into carbonic anhydride and anthranilic acid. This decomposition offers a convenient method of preparing anthranilic acid.

P. P. B.



**Betaïnes.** By H. SILBERSTEIN (*Ber.*, **17**, 2660—2665).—When phenylbetaïne hydrochloride is heated at about 100°, it splits up into dimethylaniline, carbonic anhydride, and methyl chloride. On heating ethylic phenylbetaïne chloride, or a mixture of ethyl chloracetate and dimethylaniline at a temperature not exceeding 130°, the following reactions take place :



The *phenylmethylglycocine hydrochloride*,  $\text{NPhMe} \cdot \text{CH}_2\text{COOH} \cdot \text{HCl}$ , obtained, forms colourless prisms readily soluble in water, less so in alcohol, and very sparingly in cold concentrated hydrochloric acid. It is decomposed by continued heating with water with evolution of carbonic anhydride and formation of dimethyl aniline hydrochloride. When a mixture of dimethylaniline (1 mol.) and chloracetamide (1 mol.) is digested in alcohol, and the solution, after concentration, precipitated with ether, *phenylbetaineamide chloride*,  $\text{NPhMe}_2\text{Cl} \cdot \text{CH}_2\text{CONH}_2$ , is obtained. This, heated to 110—120°, yields methyl chloride and *phenylmethylglycocineamide*,  $\text{NPhMe} \cdot \text{CH}_2\text{CONH}_2$ , which is sparingly soluble in cold, moderately in hot water and in alcohol, from which it crystallises in silky prisms or scales melting at 163°; it sublimes when carefully heated, but, on distillation, is decomposed into ammonia, dimethylaniline, and other products; when boiled with alkalis, it yields phenylmethylglycocine. *Phenylmethylglycocineamide hydrochloride* forms colourless prisms, readily soluble in water, more sparingly in alcohol. Phenylmethylglycocineamide is also produced when methylaniline and chloracetamide are heated together, and the hot aqueous solution precipitated by ammonia.

When dichloroacetic acid is heated with dimethylaniline, it apparently breaks up into carbonic anhydride and dichloromethane, whilst trichloroacetic acid yields chloroform and carbonic anhydride. In the latter reaction, an intermediate product can be obtained (probably  $\text{NPhMe}_2\text{Cl} \cdot \text{CCl}_2\text{COOH}$ ).

Diethylaniline and methyldiphenylamine when heated with chloracetamide yield neither ethylic nor methylic chloride. The above reaction with trichloroacetic acid, however, may be effected not only by means of dimethylaniline, but also by diethylaniline, methyldiphenylamine, quinoline, and pyridine. A. K. M.

#### Action of Benzaldehyde on Nitromethane and Nitro-ethane.

By B. PRIEBS (*Annalen*, **225**, 319—364).—The preparation of *phenyl-nitroethylene*,  $\text{CHPh} : \text{CHNO}_2$ , by the action of nitromethane on benzaldehyde in the presence of zinc chloride has been previously described by the author (*Abstr.*, 1884, 313). The formation of this compound may serve as a reaction for the detection of nitromethane. For this purpose the dilute solution, supposed to contain nitromethane, is mixed with sodium hydroxide, and well shaken with an excess of benzaldehyde. The unaltered benzaldehyde is removed by extraction with ether, and a current of air is passed through the solution to expel the last traces of ether. On adding dilute sulphuric

acid, a crystalline precipitate of phenylnitroethylene indicates the presence of nitromethane. Phenylnitroethylene is identical with Simon's nitrostyrene (*Annalen*, **31**, 269). It may therefore be prepared by the action of nitric acid, or better, of nitrous anhydride on a cold ethereal solution of styrene. Phenylnitroethane yields benzoic acid on oxidation. With nitrous acid, it exhibits the nitrolic acid reaction. At 85°, sulphuric acid (diluted with one-third its volume of water) decomposes phenylnitroethane into hydroxylamine, benzaldehyde, and carbonic oxide, and strong hydrochloric acid splits it up into phenylchloroacetic acid and hydroxylamine. On exposure to the light, phenylnitroethylene undergoes a gradual transformation into isophenylnitroethylene, which is deposited from alcohol in rhombic needles or plates melting between 172° and 180°. *Phenylnitroethylene dibromide*,  $\text{CHBrPh} \cdot \text{CHBr} \cdot \text{NO}_2$ , prepared by adding bromine to a solution of phenylnitroethylene in carbon bisulphide, crystallises in the monoclinic system, namely, in a combination of  $0\text{P}$  with  $\infty\text{P} \cdot \infty\text{P}$  and  $\text{P}\infty$ ;  $\beta = 83^\circ 54'$ ;  $a : b : c = 1.2568 : 1 : 1.3960$ . The crystals dissolve freely in chloroform, benzene, and carbon bisulphide, and are decomposed, by boiling with alcohol, into hydrobromic acid and phenylbromonitroethylene,  $\text{CBrPh} : \text{CHNO}_2$ . The latter compound is more easily prepared by the action of soda instead of alcohol. It crystallises in iridescent golden needles or plates which melt at 67°.

When chlorine is passed into a solution of phenylnitroethylene dissolved in chloroform, the *dichloride*,  $\text{CHClPh} \cdot \text{CHCl} \cdot \text{NO}_2$ , is obtained as a thick syrup, which crystallises with difficulty; the crystals melt at 30°. *Phenylchloronitroethylene*,  $\text{CClPh} : \text{CHNO}_2$ , is deposited from light petroleum in golden plates or needles which melt at 48°.

On nitration, phenylnitroethylene yields two isomeric nitro-products; if the acid is cooled in a freezing mixture, the *para*-derivative is mainly formed, but at a temperature of 25° a considerable quantity of the *ortho*-derivative is produced.

*Paranitrophenylnitroethylene*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{NO}_2$ , has been previously prepared by Friedländer and Mähly (*Ber.*, **16**, 848), from paranitrocinnamic acid. It unites with bromine, forming a dibromide melting at 102°; this crystallises in colourless plates, soluble in benzene and in glacial acetic acid. The *orthonitro*-compound is much more soluble in alcohol and other solvents than the *para*-derivative. It forms needle-shaped crystals melting at 106°, which turn brown on exposure to the light. The dibromide also crystallises in needles melting at 90°, which dissolve freely in chloroform, benzene, and in hot acetic acid.

*Phenylnitropropylene*,  $\text{CHPh} : \text{CMe} \cdot \text{NO}_2$ , is prepared by the action of zinc chloride on a mixture of benzaldehyde and nitroethane. The yield is by no means so good as in the case of phenylnitroethylene, as benzamide and resinous bye-products are also formed. Phenylnitropropylene resembles the ethylene compound in many of its properties. It readily crystallises in rhombic prisms which melt at 64°. It yields benzoic acid on oxidation, and is decomposed by boiling alkalis into benzaldehyde and nitroethane. The *dibromide*,  $\text{CHBrPh} \cdot \text{CBrMe} \cdot \text{NO}_2$ ,

forms transparent prisms which melt between  $77^{\circ}$  and  $78.5^{\circ}$ . This compound is not decomposed by alkalis.

*Paranitrophenylnitropropylene* forms yellow needle-shaped crystals which melt at  $114^{\circ}$ . The *orthonitro*-product forms pale yellow plates which are much more soluble in alcohol than the *para*-compound. The crystals melt at  $76^{\circ}$ .  
W. C. W.

**Paracarvacrotic Aldehyde.** By E. NORDMANN (*Ber.* 17, 2632—2634).—This aldehyde is obtained from carvacrol together with some secondary products, by means of the chloroform reaction. It crystallises in white, flat, silky scales, melts at  $96^{\circ}$ , is insoluble in cold, sparingly soluble in hot water, readily in alcohol, ether, benzene, and chloroform, also in dilute sulphuric acid with greenish-yellow coloration. It gives no characteristic colour with ferric chloride, and from this it is concluded that the group COH has taken up the *para*- and not the *ortho*-position in reference to the hydroxyl group. The formula of *paracarvacrotic aldehyde* is therefore



Like parathymotic aldehyde (*Abstr.*, 1884, 56), it does not combine with the hydrogen alkaline sulphites, but yields crystalline compounds with aniline and phenylhydrazine.  
A. K. M.

**Action of Bromacetophenone on Amides.** By F. O. BLÜMLEIN (*Ber.*, 17, 2578—2581).—On heating bromacetophenone with amides, there are formed neither the amides of acetophenone, nor isoindoles derived from them by the abstraction of a molecule of water, but substances which differ from the latter class in containing about 2 per cent. less carbon than that required by theory.

Thus, if bromacetophenone be heated with acetamide, there is formed a basic substance crystallising in long needles; this melts at  $45^{\circ}$ , boils at  $241$ — $242^{\circ}$ , and is easily soluble in alcohol and ether. Its hydrochloride forms a white crystalline powder.

The corresponding compound obtained with formamide forms a crystalline mass, and the benzamide compound forms crystals which melt at  $103^{\circ}$  and boil at  $339^{\circ}$ . It is proposed to investigate more closely the constitution of these substances.  
V. H. V.

**Preparation of Salicylic Acid.** (*Dingl. polyt. J.*, 254, 231.)—On heating diphenyl carbonate with sodium phenate, basic sodium silicylate is produced, in addition to phenol and diphenyl ether. (*Chemische Fabrik auf Actien*, formerly E. Schering, Berlin.) To prepare salicylic acid, 50 kilos. of diphenyl carbonate is heated with 54 of sodium phenate for 6 hours at  $160$ — $170^{\circ}$ , with constant agitation; the salicylic acid being subsequently extracted from the saline product.

D. B.

**Brominated Phthalic Acids.** By F. O. BLÜMLEIN (*Ber.*, 17, 2485—2497).—When  $\alpha$ -naphthol is treated with excess of bromine, a compound is formed containing six bromine-atoms in the molecule. This is very unstable and is probably a dibromo-additive product of tetrabromonaphthol,  $\text{C}_{10}\text{H}_3\text{Br}_4.\text{OH},\text{Br}_2$ , or a tetrabromo-additive pro-

duct of Biedermann's dibromo- $\alpha$ -naphthol (*Ber.*, **6**, 1119). The author has not further investigated this compound, but has studied the bromination of  $\alpha$ -naphthol in the presence of aluminium bromide. In this way, the author obtained a *pentabromo- $\alpha$ -naphthol*,  $C_{10}H_2Br_5.OH$ , which melts at 238—239°, crystallises in pale straw-coloured needles, and is almost insoluble in alcohol and ether, and only sparingly soluble in boiling benzene, xylene, or cumene. The yield was about 90 per cent. of the theoretical. This compound dissolves in alkalis to form metallic compounds:  $C_{10}H_2Br_5.ONa$  crystallises in long needles, soluble in alcohol and water;  $C_{10}H_2Br_5.OK$  in small colourless needles sparingly soluble in water.

When oxidised with dilute nitric acid (one part  $C_{10}H_2Br_5.OH$  to 10 parts acid of sp. gr. 1.15) at 100°, pentabromo- $\alpha$ -naphthol yields *tetrabromo- $\alpha$ -naphthaquinone*,  $C_{10}H_2Br_4.O_2$ . This compound crystallises in golden-yellow scales which melt at 265° to a dark liquid. It can be sublimed with care, and is soluble in glacial acetic acid and in benzene, sparingly so in alcohol and ether. It is isomeric with the tetrabromo- $\beta$ -naphthaquinone obtained by Flessa (*Inaug. Dissert.*, Zurich, 1884). If the oxidation of the pentabromonaphthol with dilute nitric acid is carried out at 150°, instead of at 100°, and the action continued for about 18 hours, *dibromophthalic acid*,  $C_6H_2Br_2(COOH)_2$ , is formed; under similar circumstances Flessa's pentabromo- $\beta$ -naphthol yielded tribromophthalic acid. Dibromophthalic acid crystallises in long aggregated needles which are easily soluble in alcohol, ether, and boiling water, sparingly in petroleum. It melts at 206°, and is converted into the anhydride. *Dibromophthalic anhydride*, obtained by sublimation of the acid, crystallises in long colourless needles melting at 208°. It is easily soluble in alcohol, sparingly so in ether and water. The salts of dibromophthalic acid, except those of the alkalis, are sparingly soluble, and contain no water of crystallisation. The *calcium salt* is deposited as an amorphous precipitate, which becomes crystalline on standing; the *barium salt* is similar to the calcium; the *silver salt* forms a flocculent precipitate soluble in much boiling water, and crystallises from this solution in small colourless plates. When the anhydride is fused with resorcinol, a brominated fluorescein appears to be formed. This compound is soluble in alkalis and in alcohol to a red solution with an intense green fluorescence.

*Action of Bromine on Orthoxylene in Presence of Aluminium.*—In this way, a tetrabromo-xylene,  $C_8Br_4.Me_2$ , was obtained, in which the bromination took place entirely in the benzene nucleus. This compound crystallises in colourless silky needles, melts at 254—255°, and distils without decomposition at 374—375°. It is easily soluble in benzene and xylene, almost insoluble in alcohol and ether. Tetrabromo-xylene is not acted on by dilute nitric acid (sp. gr. 1.15) below about 250—270°, and then the oxidation is only partial. Nitric acid of sp. gr. 1.20 effects the oxidation at 180—200°, but the product consists of a mixture of *tetrabromophthalic* and *tribromomononitrophthalic acids*, the complete separation of which could not be effected. If 5 grams of tetrabromo-xylene are heated at 170° with 50 c.c. of nitric acid of sp. gr. 1.15 and about 10 grams of bromine, *tetrabromo-*

*phthalic acid* is alone produced. This crystallises in small needles, very sparingly soluble in the usual solvents. At  $266^{\circ}$  it melts and is converted into the anhydride. *Tetrabromophthalic anhydride*, obtained by sublimation of the acid, forms small glistening needles which melt at  $258\text{--}259^{\circ}$ , and are almost insoluble in the usual solvents. The *alkaline tetrabromophthalates* are easily soluble, the salts of the other metals sparingly soluble or insoluble. The *barium* and *calcium* salts form white crystalline powders. When fused with resorcinol, tetrabromophthalic acid yields a brominated fluorescein isomeric with eosin. This compound is soluble in alkalis to a dark red solution showing intense green fluorescence.

From the above results, it is clear that in the pentabromonaphthol formed by the action of bromine on  $\alpha$ -naphthol in the presence of aluminium bromide, the three hydrogen-atoms of the nucleus containing the hydroxyl have all been replaced by bromine, but the position of the remaining two bromine-atoms in the other nucleus is uncertain. In the tetrabromo-xylene all the bromine-atoms are in the benzene-ring.

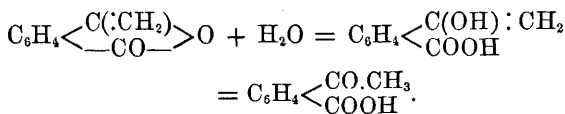
L. T. T.

**Constitution of Phthalylacetic Acid.** By S. GABRIEL (*Ber.*, **17**, 2521—2527).—When phthalylacetic acid is distilled in a vacuum, carbonic acid is evolved, and the distillate comprises a yellowish-white semi-solid mass. If a current of steam is driven through this mass, the distillate deposits small shining rhombic prisms, which melt at  $58\text{--}60^{\circ}$ , have an odour resembling that of phthalide, and are soluble in water. On keeping, however, they gradually polymerise to a yellow vitreous and odourless mass. Some of this polymerised body is always formed in the retort when the white substance is distilled with steam. It is partly reconverted into the original volatile compound by distillation in a vacuum. The freshly prepared volatile compound has the composition  $C_9H_6O_2$ , and its constitution must therefore be either

(a)  $C_6H_4\langle\begin{smallmatrix} CO \\ CO \end{smallmatrix}\rangle CH_2$ , or (b)  $C_6H_4\langle\begin{smallmatrix} -C=CH_2 \\ CO \end{smallmatrix}\rangle O$  This compound can

also be obtained from the resinous bye-products obtained during the preparation of phthalylacetic acid. When treated with bromine, this compound absorbs  $Br_2$ , yielding a crystalline substance,  $C_9H_6Br_2O_2$ , melting at  $98\text{--}99^{\circ}$ . The original volatile substance must therefore be *methylenephthalide*, and have the formula (b), and the bromoderivative must be *methylenephthalide bromide*,  $C_6H_4\langle\begin{smallmatrix} CBr.CH_2Br \\ CO \end{smallmatrix}\rangle O$

When gently warmed with potash, methylenephthalide is converted into *acetophenonecarboxylic acid*; probably according to the equations



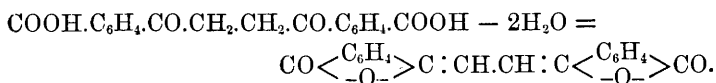
If the dibromide is boiled with water, it gives up hydrobromic acid

and yields a *methylenephthalide oxide*,  $C_8H_6O_3$ . This crystalline compound melts at  $144-146^\circ$ , and is identical with that previously obtained from acetophenonecarboxylic acid (Abstr. 1878, 734).

Phthalylbromacetic acid, when similarly treated, yields a compound which is identical with *bromomethylenephthalyl*, previously obtained by bromination of acetophenonecarboxylic acid (*loc. cit.*). The name of this compound should therefore be changed to *bromo-methylenephthalide*, and its formula would be  $C_6H_4<\begin{smallmatrix} C:CHBr \\ -CO- \end{smallmatrix}>O$ .

The compound previously described as benzylidenephthalyl also forms a crystalline *dibromide* melting at  $146^\circ$ , and should therefore be called *benzylidenephthalide*; its formula is  $C_6H_4<\begin{smallmatrix} C:CHPh \\ -CO- \end{smallmatrix}>O$ . The dibromide, when boiled with alcohol, is converted into the crystalline compound  $C_{15}H_{10}O_2Br.OEt$ , which melts at  $149^\circ$ . L. T. T.

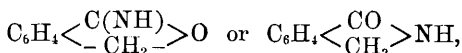
**Phthalyl Derivatives; Conversion of Ketonic Acids into Lactones.** By W. ROSER (*Ber.*, 17, 2619—2622).—When ethylenebenzoylorthocarboxylic acid is dissolved in about 15 parts of concentrated sulphuric acid, and the solution allowed to remain for some time in the cold, slender yellow needles of ethinediphthalyl separate:



When a solution of benzoylacetorthocarboxylic acid in concentrated sulphuric acid is precipitated with water, phthalylacetic acid is obtained, as observed by Gabriel (*Ber.*, 17, 2526), but this acid melts above  $260^\circ$  according to the author, and at about  $276^\circ$  decomposes with evolution of gas. By similar treatment, acetophenoneorthocarboxylic acid yields a compound melting at  $213-215^\circ$ , insoluble in water and cold alkalis, sparingly soluble in alcohol, and readily in acetic acid, from which it crystallises in colourless scales. It is perhaps a polymeride of Gabriel's phthalidimethylene,  $C_8H_6O_2$ . It may be concluded from these experiments that acids containing the group  $:CH.CO.C_6H_4.COOH$  [1 : 2] are converted into lactones by concentrated sulphuric acid. When ethylenebenzoylorthocarboxylic acid is heated with 10 parts concentrated hydrochloric acid in a sealed tube, the product washed with water and extracted with boiling alcohol, a residue of ethinediphthalyl remains, whilst the alcoholic solution contains the anhydride  $C_2H_4<\begin{smallmatrix} CO.C_6H_4.CO \\ CO.C_6H_4.CO \end{smallmatrix}>O$ . This is insoluble in water and cold alcohol, but crystallises from hot alcohol in slender silky needles melting at  $230-231^\circ$ . It agrees in its properties with the compound obtained by Gabriel by heating the diketonic acid. A. K. M.

**Reduction of Phthalimide and Phthalide.** By C. GRAEBE (*Ber.*, 17, 2598—2600).—By the action of tin and hydrochloric acid, phthalimide is converted into a base of the composition  $C_8H_7NO$ , which

crystallises in needles melting at  $150^{\circ}$ , and boiling at  $337^{\circ}$ ; it is soluble in alcohol and ether, sparingly soluble in water. From its ready formation, and its reconversion into phthalide, one of the following formula can be assigned to it:



the former of which the author considers the more probable, and assigns to it the name *phthalidine*. With sodium nitrite, it forms a *nitroso-derivative*,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{C}(:\text{N}\cdot\text{NO}) \\ \text{CH}_2 \end{smallmatrix} > \text{O}$ , which crystallises in golden needles melting at  $156^{\circ}$ , sparingly soluble in water, readily soluble in hot alcohol; on heating it with soda, it is converted into the mon-hydroxyl-derivative of methylbenzoic acid,  $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{COOMe}$ .

Phthalimide is converted into phthalide by treatment with tin and hydrochloric acid, and the addition of sodium nitrite to the product. The nitroso-derivative separates out, and phthalide is obtained on precipitating its alkaline solution with acid. Through the intermediate formation of this substance, phthalic acid may be converted into orthoxylenes.

V. H. V.

**Constitution of the Benzenetetracarboxylic Acids.** By O. JACOBSEN (*Ber.*, 17, 2516—2518).—In order to determine the constitution of the three benzenetetracarboxylic acids, the author prepared two of them by the oxidation of durenene,  $\text{C}_6\text{H}_2\text{Me}_4$ , [1 : 2 : 4 : 5], and isodurenene [1 : 2 : 3 : 5]. Durenene was first boiled with dilute nitric acid, and thus converted into a mixture of durylic and cumidic acids, and this mixture was then oxidised with permanganate. The tetrabasic acid thus obtained proved to be *pyromellitic acid*. By similar treatment, isodurenene yielded *mellophanic acid*. The constitution of the three isomeric acids, therefore, must be:—Pyromellitic acid,  $\text{C}_6\text{H}_2(\text{COOH})_4$  [1 : 2 : 4 : 5]; mellophanic acid, [1 : 2 : 3 : 5]; and phrenitic acid, [1 : 2 : 3 : 4].

L. T. T.

**Action of Sulphuric Acid on Acetophenoneorthocarboxylic Acid.** By S. GABRIEL (*Ber.*, 17, 2665—2668).—When concentrated sulphuric acid (15 grams) is added to acetophenoneorthocarboxylic acid (1 gram), an amber-coloured solution is obtained; this is allowed to remain for 24—48 hours and then poured into water, when a brown resinous substance (A) separates. The filtrate yields a further separation of a fine white powder (B) on standing. The substance A forms (after purification) dense, yellow, pointed crystals melting at  $215\text{--}216\cdot5^{\circ}$ , sparingly soluble in alcohol, insoluble in alkali and in ammonia. Its formula is  $\text{C}_{18}\text{H}_{12}\text{O}_4$ . When it is heated at  $150\text{--}160^{\circ}$  with hydroxylamine hydrochloride and alcohol, it yields an oximido-derivative,  $\text{C}_{18}\text{H}_{12}\text{O}_3\cdot\text{NOH}$ .

The second substance (B) is readily soluble in alcohol, glacial acetic acid, and in fixed and volatile alkali, from which it can be precipitated by the addition of an acid; it melts at  $132\text{--}135^{\circ}$ . Its formula,  $\text{C}_{18}\text{H}_{14}\text{O}_5$ , indicates that it is formed by the abstraction of one

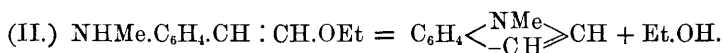
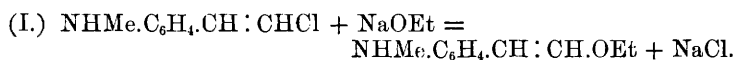
mol.  $\text{H}_2\text{O}$  from 2 mols. acetophenoneorthocarboxylic acid. This substance is a monobasic acid (*diacetophenonecarboxylic acid*), as shown by the composition of the silver salt,  $\text{C}_{18}\text{H}_{13}\text{O}_5\text{Ag}$ , and the barium salt,  $(\text{C}_{18}\text{H}_{13}\text{O}_5)_2\text{Ba}$ . When it is heated for some time above its melting point, it is converted into the compound  $\text{C}_{18}\text{H}_{12}\text{O}_4$ .

A. K. M.

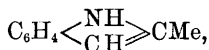
**Preparation of Isatin.** (*Dingl. polyt. J.*, **254**, 232.)—The preparation of this substance forms the subject of a patent taken out by the *Farbenfabriken*, late F. Bayer and Co. Instead of converting the products of the reaction of dichloroacetic acid with aromatic amines directly into isatin, it is proposed to subject them to a process of oxidation, it having been found that during the reaction and the subsequent process of purification oxidation by atmospheric oxygen takes place, and that the yield of imesatin, or substituted imesatins, depends on the extent of this oxidation process.

D. B.

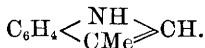
**Methylated Indoles.** By A. LIPP (*Ber.*, **17**, 2507—2511).—*Orthomethylamidochlorostyrene*,  $\text{CHCl} : \text{CH}.\text{C}_6\text{H}_4.\text{NHMe}$ , was prepared by treating an alcoholic solution of amidochlorostyrene with the calculated quantity of methyl iodide. It is heavier than water, is easily soluble in alcohol and ether, very sparingly so in water. It is liquid at ordinary temperatures, may be distilled with steam, but not alone. It dissolves in hydrochloric acid to form a hydrochloride which crystallises in small needles. When heated with sodium ethylate at  $130$ — $140^\circ$ , orthomethylamidochlorostyrene yields the same methylindole which Fischer and Hess obtained from methylphenylhydrazinepyrrolic acid (*Abstr.*, 1884, 1180). This reaction proves the correctness of the formula proposed for this body by Fischer and Hess, as its formation must take place according to the equations—



Baeyer and Jackson's methylketole has the formula



so that skatole, the remaining methylindole containing the methyl group in the side-chain, must be represented by the formula



L. T. T.

**Tolane Tetrachloride.** By L. GATTERMANN (*Ber.*, **17**, 2601).—Schüpphaus recently referred to a compound obtained by the action of chlorine on boiling toluene (*Abstr.*, 1884, 52), and it was thought probable that this might be a new dichlortoluene. The author finds, however, that the substance in question is tolane tetrachloride,  $\text{CPhCl}_2.\text{ChlPCl}_2$ , which was obtained in the same way by Liebermann and Homeyer (*Abstr.*, 1880, 259).

A. K. M.



**A New Method of Preparing Secondary Amidoazo-derivatives.** By R. HENRIQUES (*Ber.*, **17**, 2668—2673).—*Ethyl-β-naphthylamine* may be prepared from β-naphthylamine, and forms a thick oil which boils without decomposition, and does not solidify in a freezing mixture; its *hydrochloride*,  $C_{12}H_{13}N.HCl$ , is sparingly soluble in cold, moderately in hot water, crystallises in scales, melts at  $235^{\circ}$ , and distils with but slight separation of hydrochloric acid. It forms a nitrosamine,  $C_{12}H_{12}N_2O$ , which melts at  $49^{\circ}$ , and yields a yellow coloration with concentrated sulphuric acid. When nitrosoethyl-naphthylamine and aniline are heated together in solution in glacial acetic acid, a violent reaction sets in, and a deep red liquid is obtained which is kept boiling for some time; this deposits *benzazoethyl-β-naphthylamine*,  $PhN_2.C_{10}H_6.NHEt$ , on cooling. The same compound is also obtained from diazobenzene and ethylnaphthylamine. It forms red needles melting at  $102-103^{\circ}$ , is insoluble in water, but yields orange-red solutions with alcohol and other solvents. With concentrated acids, it gives bluish-violet salts which are decomposed by water. It yields a *nitrosamine* which forms ruby-coloured crystals melting at  $97^{\circ}$ ; when this is treated with aniline in glacial acetic acid, the nitroso-group is removed and the amidoazo-compound reproduced.

Nitrosoethylnaphthylamine reacts with ortho- and para-toluidine in the same way as with aniline, the compounds obtained melting respectively at  $132^{\circ}$  and  $112-113^{\circ}$ . With amidoazobenzene, it forms *azobenzeneazoethyl-β-naphthylamine*,  $PhN_2.C_6H_4.N_2.C_{10}H_6.NHEt$ , which, for comparison, has also been prepared from diazoazobenzene and ethylnaphthylamine. It forms small cherry-red crystals, melts at  $141-142^{\circ}$ , and gives a deep blue colour with sulphuric acid. The reaction with diamines is apparently less simple; metaphenylenediamine and tolylenediamine give brownish-red dye-stuffs with the nitrosamine, whilst paraphenylenediamine gives no colour reaction. Methylamine and phenylhydrazine do not react with nitrosoethyl-naphthylamine. Experiments in which the nitrosamine was treated with aminesulphonic acids yielded negative results; no combination occurs in glacial acetic acid solution, but if hydrochloric acid is added colouring matters are formed.

Streiff's nitrosophenyl-β-naphthylamine (*Annalen*, **209**, 157), when submitted to the above reaction with aniline, yields *benzeneazophenyl-β-naphthylamine*,  $C_{22}H_{17}N_3$ , corresponding with the ethyl-compound. It forms compact dark-red needles of metallic lustre, melting at  $128-129^{\circ}$ ; the mother-liquor contains phenylnaphthylamine, this reformation of the amine constituting the chief reaction in the case of the other nitrosamines which the author has examined. Nitrosoethyl-α-naphthylamine and aniline yield, for instance, amidoazobenzene, ethylnaphthylamine, and a little *benzeneazoethyl-α-naphthylamine*,  $C_{18}H_{17}N_3$ ; this is a stronger base than the β-compound, forms large, bright-red, transparent crystals, melting at  $58-59^{\circ}$ , and yields salts crystallising readily in violet needles; it gives a bluish-violet colour with sulphuric acid. Nitrosodiphenylamine and aniline (see also *Ber.*, **10**, 1309) yield diphenylamine as the chief product, also amidoazobenzene and a small quantity of phenylamidoazobenzene. Similar

results are obtained from nitrosomethylaniline and aniline. In the action of aniline on the nitrosamines of more complex substances, such as carbazole and tetrahydroquinoline, the NO group is eliminated and the amine is reproduced. A. K. M.

**Nitrosonaphthol and its Derivatives.** By M. ILINSKI (*Ber.*, **17**, 2581—2593).— $\alpha$ -Nitroso- $\beta$ -naphthol is best prepared from  $\beta$ -naphthol by the process suggested by Stenhouse and Groves (comp. Trans., 1884, 294); in addition to its properties described by former workers, the author finds that it is volatile in a current of steam when pure, but if impure it forms resinous matters.

Its potassium-derivative,  $C_{10}H_6NO_2K$ , crystallises in metallic, glistening leaflets, soluble in water. Its *ammonium* salt, crystallising in the same form, is stable only in an atmosphere of ammonia; on boiling a solution of the ammonium salt, the corresponding amido-derivative, is formed. Its *silver* salt forms a red-brown powder, insoluble in water and alcohol; the *silver-ammonium* salt crystallises in delicate green needles, and the *hydrogen-silver* salt forms a microscopic crystalline precipitate. By the action of methyl iodide on the normal silver salt, there is obtained the *methyl ether* of  $\alpha$ -nitroso- $\beta$ -naphthol,  $C_{10}H_6NO_2Me$ , which crystallises in long prismatic needles melting at  $75^\circ$ , dissolving in concentrated sulphuric acid with formation of a red colour.

$\alpha$ -Nitroso- $\alpha$ -naphthol is best prepared from  $\alpha$ -naphthol, together with its isomeride  $\beta$ -nitroso- $\alpha$ -naphthol, by the process of Stenhouse and Groves mentioned above: the two compounds are then separated by the difference of their solubility in dilute soda solution. The resultant  $\alpha$ -nitroso- $\alpha$ -naphthol melts with decomposition at  $190^\circ$ . Its salts are comparatively unstable, and even on agitation with ether are reconverted into the original substance. The potassium, sodium, calcium, barium, and magnesium salts are readily soluble in water. On the addition of silver nitrate to a solution of the last-named salt there is precipitated a red-brown resin, which on purification and subsequent treatment with methyl iodide can be converted into the *methyl ether* of  $\alpha$ -nitroso- $\alpha$ -naphthol, which crystallises in needles, melting probably at about  $100^\circ$ . It is readily soluble in alcohol, ether, and benzene, but insoluble in water.  $\alpha$ -Nitroso- $\beta$ -naphthol and  $\beta$ -nitroso- $\alpha$ -naphthol differ in their reaction with cobalt chloride; the former yields a cobalt-derivative, containing no chlorine and unaltered by acids, alkalis, oxidising and reducing reagents, whilst the latter yields no such compound.

By the action of ammonia on  $\alpha$ -nitroso- $\beta$ -naphthol a substance of the formula  $C_{10}H_6N_2O$  is formed; this was considered to be a nitroso-amidonaphthalene,  $C_{10}H_6NO.NH_2$ , but is more probably a quinon-oximine. V. H. V.

**$\alpha$ - and  $\beta$ -Hydrojuglone.** By F. MYLIUS (*Ber.*, **17**, 2411—2414).—The earlier writers on the subject all regard juglone as occurring ready formed in the green shell of the walnut, the author, however, finds that this view is incorrect, and that it is formed by the oxidation of two isomeric crystalline bodies,  $\alpha$ - and  $\beta$ -hydrojuglone, standing in

the same relation to it as that of the dihydroxybenzenes to quinone. Those substances occur in all the green parts of the walnut tree, but the shells of the *ripe* nuts do not contain even a trace of hydrojuglones. No account of the method of preparation is given.

*α-Hydrojuglone*,  $C_{10}H_8O_3$ , forms colourless plates, melts at  $168-170^\circ$ , is soluble in about 200 parts of water at  $25^\circ$ , is readily soluble in alcohol and ether, insoluble in chloroform; it is readily soluble in alkalis with yellow colour, turning quickly to red on exposure to air. Ferric chloride or bromine-water oxidises it to juglone. On reducing juglone, *α*-hydrojuglone is alone formed.

*Acetyl-α-hydrojuglone*,  $C_{10}H_8O_3Ac_3$  formed by digestion of *α*-hydrojuglone with acetic anhydride, melts at  $124^\circ$ . A solution of *α*-hydrojuglone or of juglone in organic bases yields nitrogenous compounds of juglone by oxidation in air. Of these compounds that with dimethylaniline,  $C_{10}H_8O_3.NMe_2Ph$ , is very readily prepared; it crystallises in lustrous red tables, and by treatment with hydrochloric acid is converted into a hydroxyjuglone of the formula  $C_{10}H_8O_3.OH$ , having the characters of a strong acid.

*β-Hydrojuglone* crystallises in colourless plates, melts at  $97^\circ$ , is soluble in about 900 parts of water at  $25^\circ$ , is sparingly soluble in alcohol and ether, readily soluble in chloroform; it is readily soluble in alkalis with yellow colour, which changes to red on exposure to air. It gives a blood-red coloration with ferric chloride, and is converted into a brominated product by bromine-water. It occurs in much smaller quantity than its isomeride.

On fusion with potash, both hydrojuglones yield phenol, salicylic acid, and metahydroxybenzoic acid.

The author had independently arrived at the same conclusion as Bernthsen (Abstr., 1884, 1365) as to juglone having the formula  $C_{10}H_6O_3$ . He further confirms Bernthsen's view that juglone is a hydroxynaphthaquinine, by showing that *α*-hydrojuglone also yields naphthalene when distilled with zinc-dust.

A. J. G.

**A Sulphoxide of Naphthalene.** By A. G. EKSTRAND (*Ber.*, 17, 2601—2604). Whilst preparing naphthonitrile by distilling a mixture of potassium *α*- and *β*-naphthalene sulphonates with potassium ferrocyanide, the author observed the formation of secondary substances which crystallise from the highest fraction of the crude nitrile. Two compounds may be separated by crystallisation from alcohol, one of which is obtained in very small quantity and forms scales melting at  $148^\circ$ ; the other crystallises in long needles, melts at  $111^\circ$ , and dissolves very readily in carbon bisulphide, ether, benzene, warm glacial acetic acid, and alcohol. Its formula appears to be  $C_{30}H_{20}SO$ . It is insoluble in acids and alkalis, and is not acted on by acetic anhydride; it readily yields a bromine-derivative, and this crystallises in colourless needles melting at  $182^\circ$ , is very readily soluble in carbon bisulphide, and very sparingly in alcohol and glacial acetic acid. The compound  $C_{30}H_{20}SO$  is probably *naphthylenedinaphthylsulphoxide*,



When its solution in glacial acetic acid is heated with potassium di-

chromate, *dinaphthylsulphoxide*,  $\text{SO}(\text{C}_{10}\text{H}_7)_2$ , is produced, and crystallises in prisms melting at  $162^\circ$ . By the action of nitric acid (sp. gr. 1.21) on naphthylenedipnaphthylsulphoxide at  $130$ – $140^\circ$ , a *dinitronaphthyl sulphide*,  $\text{S}(\text{C}_{10}\text{H}_6\text{NO}_2)_2$ , is obtained, crystallising in small golden yellow prisms melting at  $230$ – $231^\circ$ . It is insoluble in alkalis, almost insoluble in alcohol and carbon bisulphide, and very sparingly soluble in glacial acetic acid. A. K. M.

**Derivatives of the Isomeric Dinaphthols.** By E. OSTERMAYER and J. ROSENHEK (*Ber.*, 17, 2453–2455).—The authors describe several derivatives of Dianin's  $\alpha$ - and  $\beta$ -dinaphthols.

*$\alpha$ -Dinaphthyl diethyl ether*,  $\text{EtO.C}_{10}\text{H}_6.\text{C}_{10}\text{H}_6.\text{OEt}$ , was prepared by acting on  $\alpha$ -dinaphthol with alcoholic potash and ethyl iodide. It crystallises in white pearly scales melting at  $211^\circ$ , and is easily soluble in hot benzene, sparingly so in ether or alcohol, insoluble in water.  *$\alpha$ -Dinaphthyl dimethyl ether*,  $(\text{C}_{10}\text{H}_6.\text{OMe})_2$ , crystallises in glistening plates melting at  $251^\circ$ .

*$\beta$ -Dinaphthyl diethyl ether*,  $(\text{C}_{10}\text{H}_6.\text{OEt})_2$ , crystallises in needles which melt at  $90^\circ$ , and are soluble in alcohol and benzene.  *$\beta$ -Dinaphthyl dimethyl ether* crystallises in double pyramids, soluble in benzene, insoluble in alcohol; it melts at  $190^\circ$ .

The authors were unable to isolate the potassium or sodium compounds of  $\alpha$ - or  $\beta$ -dinaphthol. These compounds are very unstable, and in all attempts at purification were either partly or wholly reconverted into the dinaphthol. Schaeffer's experiences with  $\alpha$ - and  $\beta$ -naphthol were similar. L. T. T.

**Ethereal Oils.** By O. WALLACH (*Annalen*, 225, 314–318).—The chief constituent of oil of cajeput is identical with cyneol. The terpenes contained in oil of bergamot and oil of eucalyptus are distinct from cynene. Oil of lemon yields a small precipitate with bromine, and a large quantity of the crystalline tetrabromide is obtained from *Oleum corticis aurantiorum*. This compound closely resembles cynene tetrabromide, but differs from it in its melting point ( $104^\circ$ ).

W. C. W.

**Oleum Cynæ.** By O. WALLACH and W. BRASS (*Annalen*, 225, 291–314).—After referring to the researches of Völkel (*Annalen*, 87, 312), Kraut (*Jahresber.*, 1862, 460), and Faust and Homeyer (this Journal, 1875, 375) on this subject, the authors describe the experiments by which they succeeded in isolating *cyneol*,  $\text{C}_{10}\text{H}_{18}\text{O}$ , and *cynene*,  $\text{C}_{10}\text{H}_{16}$ , from the crude oil. The separation depends on the fact that cyneol forms an unstable crystalline compound,  $(\text{C}_{10}\text{H}_{18}\text{O})_2.\text{HCl}$ , when it is treated with the hydrochloric acid gas. This substance is decomposed by water into hydrochloric acid and cyneol. It is decomposed also when heated in sealed tubes, yielding cynene, water, and hydrochloric acid.

Pure cyneol boils at  $176$ – $177^\circ$ , and has no action on polarised light. Its sp. gr. is 0.92297 at  $16^\circ$ . It is oxidised to oxalic acid by nitric acid sp. gr. 1.15. Cyneol also forms an unstable crystalline compound with hydrobromic acid, and with hydriodic acid it yields the iodide  $\text{C}_{10}\text{H}_{18}\text{I}_2$ , which crystallises in transparent rhombic plates. The iodide is decomposed by heat into cynene and hydriodic acid.

By slowly dropping bromine into a well-cooled mixture of light petroleum and cyneol or rectified *oleum cynæ*, an additive product,  $C_{10}H_{18}O, Br_2$ , is obtained, which crystallises in red prisms. If the crystals are placed in a sealed tube and kept in a cool place, they slowly decompose, forming a colourless liquid, which in the course of time deposits a crystalline mass. By recrystallisation from chloroform, *cynene tetrabromide*,  $C_{10}H_{18}Br_4$ , is obtained in rhombic crystals melting at  $125.5^\circ$ .

*Cyneol diiodide* is formed when iodine acts on cyneol diluted with light petroleum. It is deposited from its ethereal solution in long needle-shaped crystals, which are more stable than those of the bromide.

Cyneol is not acted on by metallic sodium, nor by sodium ethylate and ethyl iodide; neither does it enter into reaction with hydroxylamine or phenylhydrazine, nor yet with phosphorus pentachloride or benzoic chloride at the ordinary temperature. These negative results indicate that the oxygen in cyneol is not present in the form of hydroxyl.

Pure cynene is best prepared by warming a mixture of the iodide,  $C_{10}H_{18}I_2$  (3 parts), with aniline (4 parts), and distilling the product in a current of steam. The hydrocarbon boils at  $181-182^\circ$ . Its sp. gr. is 0.85384 at  $16^\circ$ . Pure cynene has a characteristic odour of lemons. When bromine is added to a well-cooled mixture of cynene and alcohol or ether, crystals of the tetrabromide are deposited. Cynene is converted into cymene by strong sulphuric acid or by phosphorus pentasulphide.

W. C. W.

**Action of the Halogen Acids on Wormseed Oil. II.** By C. HELL and A. RITTER (*Ber.*, 17, 2609—2614).—The action of hydrochloric acid has been described (*Abstr.*, 1884, 1363). When hydrobromic acid acts on wormseed oil in the cold, a crystalline substance is obtained, and is apparently the additive product  $C_{10}H_{18}O, HBr$ , corresponding with the hydrochloric acid additive product previously described (*loc. cit.*). It is, however, much less stable than the latter compound, and rapidly deliquesces and becomes brown on exposure to the air. It melts between  $33^\circ$  and  $35^\circ$ . A *cynene dihydrobromide*,  $C_{10}H_{18}Br_2$ , may also be obtained, corresponding with the dihydrochloride. This crystallises in white silky scales, melts at  $64^\circ$ , and is decomposed by heat into cynene and hydrobromic acid, as also when boiled with water or dilute alkalis. By the action of hydriodic acid on wormseed oil in the cold, crystals may likewise be obtained, but the compound is so unstable that it could not be isolated. The further action of hydriodic acid yields *cynene dihydriodide*,  $C_{10}H_{18}I_2$ , which crystallises in short white needles melting at  $76-77^\circ$ , and is even less stable than the dihydrobromide. It can be kept for three or four days only, even in the dark, and in a sealed tube. When heated with zinc-dust and water, *dihydrocynene*,  $C_{10}H_{18}$ , is obtained, boiling at  $166-167^\circ$ . This is a colourless strongly refracting oil, resembling cynene in its odour. It may also be obtained from the dihydrochloride.

On comparing the properties of the dihydrochlorides, bromides, and iodides of the terpenes with those of the corresponding cynene-

derivatives, striking resemblances are observed. The dihydrochlorides of many of the terpenes melt, for instance, at nearly the same temperature as cynene dihydrochloride. Further experiments are, however, necessary to decide whether these terpenes are identical or isomeric with cynene.

A. K. M.

**The so-called Campholenic Acid.** By J. KACHLER and F. V. SPITZER (*Ber.*, **17**, 2400—2401).—The authors regard the compound,  $C_{10}H_{16}O_2$ , recently described by Goldschmidt and Zürrer (*Abstr.*, 1884, 1364) under the name of campholenic acid, as identical with the substance termed by them hydroxycamphor, formed by the action of sodium amalgam on  $\beta$ -dibromocamphor. They consider the constitution of this substance to be still unsettled, and will continue their researches on it.

A. J. G.

**Coal-tar Quinoline.** By M. C. TRAUB and C. SCHARGES (*Ber.*, **17**, 2618—2619).—In preparing quinophthalone from coal-tar quinoline, a red resinous substance is also produced which, however, is not formed when pure quinaldine or a mixture containing only quinoline and quinaldine is employed. When coal-tar quinoline (b. p.  $235^\circ$ ) is heated with a little phosphorus pentoxide, it assumes a more or less intense reddish coloration, and on dissolving the product in water or alcohol, the solution obtained shows a splendid yellowish-green fluorescence. Neither Skraup's quinoline nor pure quinaldine yield this reaction. The fractions of coal-tar quinoline distilling below  $200^\circ$  behave like pure quinoline and quinaldine, whilst the portion distilling below  $230^\circ$  yields a feeble reaction.

The above is a convenient method of recognising coal-tar quinoline. The reaction indicates the presence of a third substance besides quinoline and quinaldine, and this the authors are trying to isolate.

A. K. M.

**$\alpha$ -Diquinoline from Azobenzene.** By A. CLAUS and P. STEGELITZ (*Ber.*, **17**, 2380—2383).—By heating a mixture of 20 grams azobenzene, 80 grams glycerol, 30 grams concentrated sulphuric acid, and 20 grams Nordhausen sulphuric acid, for two days on the water-bath, there are obtained  $\alpha$ -diquinoline (2 grams) and benzidine sulphate (6 grams).

By dissolving  $\alpha$ -diquinoline in fuming nitric acid, heating on the water-bath, and precipitating with water, nearly colourless, slender needles are obtained. These decompose without fusion at  $260^\circ$ , do not yield compounds with acids, and appear to consist of a mixture of nitration products.

A. J. G.

**Synthesis of  $\alpha$ -Diquinoline.** By E. OSTERMAYER and W. HENRICHSEN (*Ber.*, **17**, 2444—2451).—This base was originally obtained by Weidel (*Abstr.*, 1882, 69) by the action of sodium on quinoline at  $192^\circ$ . The authors find that it can also be prepared from benzidine by Skraup's reaction. For this purpose, benzidine sulphate (50 grams), nitrobenzene (25 grams), sulphuric acid (100 grams), and glycerol are slowly heated in a reflux apparatus, care being taken that the reaction does not become unmanageable. The yield of diquinoline

is very good (about 33 per cent. of the benzidine sulphate employed), but its purification is rendered difficult by tar-like products simultaneously formed; by substituting para- or ortho-nitrophenol for the nitrobenzene, however, there is obtained not only a much larger yield (about 72 per cent. of the benzidine sulphate), but from the absence of the tar-like products the purification is very easily effected.

*Diquinoline nitrate* is nearly insoluble in water. The *aurochloride*,  $C_{18}H_{12}N_2 \cdot HAuCl_4 + 2H_2O$ , crystallises in very slender needles and is very sparingly soluble. The *stannichloride*,  $C_{18}H_{12}N_2 \cdot H_2SnCl_4$ , crystallises in colourless needles. The *methiodide*,  $C_{18}H_{12}N_2(MeI)_2$ , was prepared by heating diquinoline with methyl iodide and methyl alcohol in sealed tubes at  $120^\circ$ . It crystallises in yellow needles. A compound with methyl chloride of like composition was also obtained. Weidel had described the methiodide as containing only 1 mol. of methyl iodide (*loc. cit.*). The compound with *methyl sulphate*,



prepared by heating diquinoline, methyl alcohol, and sulphuric acid in sealed tubes at  $180^\circ$ , crystallises in colourless needles. Its dilute aqueous solution shows a bluish-violet fluorescence and gives a blood-red coloration with alkalis.

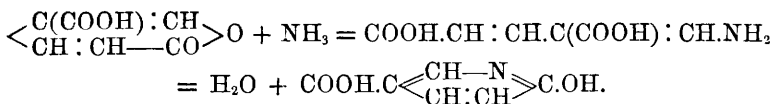
Diquinoline unites directly with bromine to form two additive compounds: an orange-yellow, apparently crystalline substance of the formula  $C_{18}H_{12}N_2Br_2$ , and a pale yellow tetrabromide,  $C_{18}H_{12}N_2Br_4$ . Both compounds are very unstable; when boiled with water, they are decomposed, diquinoline being in part regenerated. By heating with hydrochloric acid at  $180-200^\circ$ , *monobromodiquinoline*,  $C_{18}H_{11}BrN_2$ , is formed amongst other products. It crystallises in tufts of needles, melts at  $150-155^\circ$ , and is readily soluble in cold alcohol. *Diquinolinechloriodide hydrochloride*,  $C_{18}H_{12}N_2Cl_2I_2 \cdot 2HCl$ , is prepared by precipitating an aqueous solution of diquinoline hydrochloride with a solution of iodine chloride.

*Diquinolinedisulphonic acid*,  $C_{18}H_{12}N_2(SO_3H)_2$ , is prepared by the action of nitrophenol, glycerol, and sulphuric acid on benzidinedisulphonic acid; it crystallises in colourless plates or needles, is sparingly soluble in water, insoluble in alcohol, and has a very bitter taste. The potassium salt has the formula  $C_{18}H_{12}N_2(SO_3K)_2 + H_2O$ . It is probably identical with the disulphonic acid prepared directly from diquinoline by Weidel.

A. J. G.

**Formation of Pyridine Derivatives. II. Condensation Products from Malic Acid.** By H. v. PECHMANN and W. WELSH (*Ber.*, 17, 2384-2395).—In a previous communication, v. Pechmann has shown that by the action of sulphuric acid on malic acid, formic acid and coumalinic acid are formed (*Abstr.*, 1884, 1124). The present paper deals with the derivatives of coumalinic acid.

By the action of ammonia or ammonium carbonate on coumalinic acid 1:4 hydroxynicotinic acid is formed. The reaction proceeds more readily if ethyl coumalinate is employed instead of the free acid. This change is most probably represented by the equation—



For although the intermediate coumalamic acid could not be isolated, yet the analogous methyl coumalanilide has been obtained. The hydroxynicotinic acid obtained is identical with Königs and Geigy's hydroxypyridinecarboxylic acid (Abstr., 1884, 1195); if heated with phosphoric chloride it is converted into *chloronicotic acid*,  $\text{C}_5\text{H}_3\text{NCl}\cdot\text{COOH}$ . This crystallises in shining plates, melts with decomposition at  $199^\circ$ , is readily soluble in water, ether, alcohol, and glacial acetic acid, sparingly soluble in chloroform and benzene. The aqueous solution gives a pale-green precipitate with cupric acetate. By reduction with tin and hydrochloric acid, it is converted into nicotic acid. As the chlorine-atom in chloronicotic acid exhibits properties shown by Friedländer and Ostermaier to be characteristic for the chlorine-atom occupying the position next to the nitrogen-atom, it follows that from its formation from hydroxyquinolinic acid, and from the known constitution of nicotic acid, that this hydroxynicotinic acid must have the constitution  $[\text{N} : \text{HO} : \text{COOH} = 1 : 2 : 5]$ .

*Monomethyl coumalanilide*,  $(\text{C}_6\text{H}_5\text{NPh})(\text{COOH})\cdot\text{COOMe}$ , is prepared by the action of aniline on methyl coumalinate. It crystallises in citron-yellow needles, melts with decomposition at  $140^\circ$ , is readily soluble in hot alcohol, chloroform, and benzene, sparingly soluble in ether, insoluble in water, and behaves as a free acid. It readily suffers decomposition by the action of water, acids, or alkalis.

*Phoxynicotinic acid*,  $\text{C}_5\text{H}_3\text{N}(\text{OPh})\cdot\text{COOH}$   $[\text{OPh} : \text{COOH} = 1 : 4]$ , is prepared by boiling methyl coumalanilide for a few minutes with soda, &c. It crystallises in lustrous white needles, melts at  $275\text{--}280^\circ$ , can be sublimed by careful heating, is soluble in hot water, alcohol, and glacial acetic acid, nearly insoluble in ether, chloroform, and benzene. By heating it with concentrated hydrochloric acid at  $200^\circ$ , a crystalline substance, probably phenoxypyridine, is obtained, whilst carbonic anhydride is evolved.

*Methoxynicotinic acid*,  $\text{C}_5\text{H}_3\text{N}(\text{OMe})\cdot\text{COOH} + \text{H}_2\text{O}$ , is obtained either by the direct methylation of hydroxynicotinic acid or by condensation from coumalinic acid and methylamine. It crystallises in flat needles of satiny lustre, melts at  $237\text{--}238^\circ$ , is nearly insoluble in cold, but very readily soluble in hot water, soluble in alcohol, ether, and glacial acetic acid, insoluble in chloroform and benzene. It has scarcely any basic properties.

A. J. G.

### Synthesis of Pyridine Derivatives. III. Coumalinic Acid.

By H. v. PECHMANN (*Ber.*, 17, 2396—2399).—*Bromocoumalinic acid*,  $\text{C}_5\text{H}_2\text{BrO}_2\cdot\text{COOH}$ , is prepared by heating a mixture of finely powdered coumalinic acid (10 parts), glacial acetic acid (30 parts), and bromine (12 parts), with a little iodine, on the water-bath. It crystallises in colourless, lustrous needles, melts at  $176^\circ$ , can be sublimed in small portions, is readily soluble in alcohol, ether, glacial acetic acid, and chloroform, more sparingly soluble in benzene, insoluble in light



petroleum. It is nearly insoluble in cold, moderately soluble in hot water, the solution soon decomposing, if boiled, with copious evolution of carbonic anhydride and formation of a substance volatile in steam, and of very penetrating odour. Like coumalinic acid, it is converted by alkalis into an acid yielding yellow salts. Ammonia gas passed into an alcoholic or ethereal solution of the acid causes the precipitation of a colourless crystalline salt. *Methyl bromocoumalinate*,  $C_5H_3BrO_2.COOMe$ , crystallises in prismatic needles, melts at  $134^\circ$ , can be distilled unaltered, is insoluble in water, sparingly soluble in ether, more readily soluble in alcohol and benzene.

*Bromhydroxynicotinic acid*,  $OH.C_5H_2NBr.COOH$  [ $OH : COOH = 1 : 4$ ], is obtained as methyl salt by slowly adding finely powdered methyl bromocoumalinate to two parts of concentrated ammonia, and separates after some time in crystals. The *free acid* is dimorphous, crystallising in long slender needles, or in strongly refractive rhombic tables. It melts at  $296^\circ$ , is sparingly soluble in boiling water, nearly insoluble in ether, alcohol, and glacial acetic acid. On boiling its aqueous solution with cupric acetate, a green precipitate is formed. The *methyl salt*,  $OH.C_5H_2NBr.COOMe$ , crystallises in colourless, flexible, asbestos-like needles, melts at  $221-222^\circ$ , and is soluble in water, alcohol, and glacial acetic acid, only when heated.

*Methyl bromophenoxy nicotinate*,  $OPh.C_5H_2NBr.COOMe$ , is formed by the action of aniline on an alcoholic solution of methyl bromocoumalinate, there being no formation of the intermediate coumanalidate as in the case of the non-brominated acid (preceding Abstract). It crystallises in lustrous white needles, melts at  $183.5^\circ$ , can be distilled unaltered, is insoluble in water, soluble in alcohol, ether, and chloroform. Its odour is peculiar, recalling that of rotten fruit. It is readily saponified by heating it with alcoholic soda.

A. J. G.

**Oxidation of Piperidine.** By C. SCHOTTEN (*Ber.*, **17**, 2544—2547).—Benzoylpiperidine was suspended in water and oxidised with potassium permanganate. *Benzoylhomopiperidic acid*,  $Ph.CO.C_5H_{10}O_2N$ , thus obtained crystallises in needles melting at  $94^\circ$  to a clear liquid, and volatilises completely at higher temperatures. It is moderately soluble in the usual reagents. It is easily soluble in ammonia or alkaline carbonates, and with these neutral solutions the heavy metals give insoluble precipitates. The acid decomposes slowly when boiled with water, more rapidly with mineral acids. Heated in closed tubes with concentrated hydrochloric acid at  $100-110^\circ$ , it splits up into benzoic acid, and the hydrochloride of a nitrogenous acid. *Homopiperidic acid hydrochloride*,  $C_5H_{11}O_2N.HCl$ , crystallises in hygroscopic rhombic plates or prisms. These crystals are doubly refracting. The platinum-chloride crystallises in easily soluble plates.

L. T. T.

**A New Oxidation-product of Conine.** By C. SCHOTTEN and J. BAUM (*Ber.*, **17**, 2548—2551).—Benzoylconine was oxidised with permanganate in a similar way to that employed by Schotten with benzoylpiperidine (preceding Abstract). *Benzoylhomococonic acid*,  $COPh.C_8H_{16}O_2N$ , thus obtained, crystallises in prisms or needles which melt at  $142-143^\circ$  to a clear liquid, and volatilises if more

strongly heated. It is very sparingly soluble in ether, easily in alcohol or ethyl acetate. When boiled with water, slight decomposition takes place. It dissolves readily in dilute ammonia or in alkaline carbonates, and forms insoluble salts with most of the heavy metals: the silver salt is an amorphous powder. When heated with hydrochloric acid in closed tubes at  $100^{\circ}$ , this acid is decomposed into benzoic acid and a nitrogenous acid now under investigation.

From the stability of conine towards oxidising agents, the authors are inclined to think that it contains the isopropyl group, and not the normal one.

L. T. T.

**Parabuxinidine, a Fourth Alkaloid from the Box Tree, *Buxus Sempervirens*.** By G. A. BARBAGLIA (*Ber.*, 17, 2655—2656).—The leaves and twigs of the box tree are extracted in the usual way, and the extract treated as previously described (*Gazzetta*, 1883, 249). The product is dissolved in alcohol, neutralised with an alcoholic solution of oxalic acid, the white precipitate boiled with water, dissolved in dilute aqueous oxalic acid, sodium carbonate added in slight excess, and the liquid extracted with ether. *Parabuxinidine* crystallises from the ethereal solution in thin, colourless, transparent, microscopic prisms. It is insoluble in water, but very readily soluble in alcohol; with oxalic acid, the alcoholic solution gives a heavy white precipitate insoluble in water and alcohol. The alkaloid contains nitrogen, melts readily, has a very bitter taste, and burns with a smoky flame.

A. K. M.

**Lupinidine from *Lupinus Luteus*.** By G. BAUMERT (*Anralen*, 225, 365—384).—In order to separate lupinine from lupinidine, the author takes advantage of the fact that lupinine sulphate dissolves freely in absolute alcohol, but the acid sulphate of lupinidine is only sparingly soluble in this solvent. The lupinine was further purified by Baeyer's process (*Landw. Versuchs-Stat.*, 14, 161). *Lupinidine platinochloride* is thrown down as an amorphous precipitate when an alcoholic solution of lupinidine hydrochloride is added to an aqueous solution of platinum chloride. This precipitate is somewhat soluble, but is redeposited from its solution in a variety of different crystalline forms, all of which belong to the rhombic system. The crystals are very slightly soluble in alcohol or hot water.

*Lupinidine hydrochloride* forms rhombic prisms which are very hygroscopic. The *aurochloride* is unstable. The *acid sulphate*,  $C_8H_{15}N, H_2SO_4$ , dissolves freely in water, but is insoluble in absolute alcohol. The *hydriodide*,  $C_8H_{15}N, HI$ , is precipitated on mixing concentrated solutions of potassium iodide and the hydrochloride. The precipitate dissolves in alcohol and hot water, and the aqueous solution deposits colourless plates containing  $\frac{1}{2}$  mol.  $H_2O$ . The free base is a thick oil, heavier than water, and has a bitter taste. It is easily attacked by oxygen, especially in presence of acids, or potash, or soda.

W. C. W.

**Albumin of the Splenic Fever Bacilla.** By M. NENCKI (*Ber.*, 17, 2605—2609).—Nencki and Schaffer (*J. pr. Chem.*, 20, 443)

showed that albuminoïd substances formed the chief component (more than 84 per cent.) of dried bacteria which had been generated in a gelatin medium. Of these albuminoids, mycoprotein formed more than 90 per cent. The albumin obtained from the splenic fever bacillus is found to contain only traces of mycoprotein, whilst the chief component resembles in its chemical behaviour vegetable casein and mucous substances. It is readily soluble in alkalis, but quite insoluble in water, acetic and dilute mineral acids. In composition it also appears to differ from mycoprotein, but, like the latter, contains no sulphur. It is named by the author *anthraxprotein*.

A. K. M.

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## Physiological Chemistry.

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**Experiments on Digestion in the Horse.** By ELLENBERGER and HOFFMEISTER (*Bied. Centr.*, 1884, 684—688).—Previous experiments of the authors were made on the digestive functions of the mouth and stomach; those now recorded refer to the intestines and their secretions; these secretions are difficult to obtain, the horse not having a gall bladder, so that the authors were compelled to use extracts of the pancreas, liver, and mucous lining of the intestine. The reaction in the fore and true stomach was always found to be decidedly acid; it is also acid in the fore part of the small intestine, but when the jejunum is reached the reaction becomes alkaline; the blind and large intestines are mostly alkaline. From experiments on three horses, it was found that it took 96 hours for the food to pass through the intestines. Only a portion undergoes a change in the stomach, the chief transformations taking place in the intestine. The contents of the stomach appear a relatively dry, crumbling mass, those of the small intestine are watery, and almost fluid; in the larger intestine, the contents take more the form of fæces, there is little starch present, but much indigestible matter. In the stomach, the activity of digestion is considerable; the albuminoids in the dry substance, when the animal is fed on oats, sink from 11.2 per cent. to 6 per cent.; the digestion in the small intestine is very active, only 23—52 per cent. undigested albumin and 38—59 per cent. undigested carbohydrates being found therein, substances which are unaffected by the secretions of the stomach being rapidly digested here. The pancreatic ferments and gall enter at the duodenum, and play a most important part in the digestion.

J. F.

**Researches on the Fermentation of Cellulose, especially with reference to its Solution in the Alimentary Canal.** By H. TAPPEINER (*Zeits. Biol.*, 20, 52—134).—The two chief propositions are as follows: 1st. In which section of the alimentary canal does the solution of cellulose take place? 2nd. Is the solution produced by an organised or an unorganised ferment? Weighed quantities from the

contents of the different sections of the alimentary canal of oxen fed with hay were placed in suitable flasks and divided into three equal portions. In the first both organised and unorganised ferments were alike destroyed by boiling the contents of the flask, this portion afterwards served for the determination of the cellulose in the sample; the 2nd part was maintained under conditions as near as possible like those in the intestine; and the 3rd part was similarly treated, only the action of the organised ferment was inhibited by the addition of antiseptics (thymol, &c.), which, at the same time, did not affect the unorganised ferment. Great difficulty was experienced in obtaining a fair sample of the paunch contents. Scarcely any solution takes place in the small intestine, about 6 per cent. in the large intestine, and a maximum of 36 per cent. in the paunch.

In order to determine whether the intestinal gases were developed from the solid or liquid contents of the intestine, the clear liquid from the filtered paunch contents was digested with fibrin, egg-albumin, starch powder, and acetate of lime; very little gas was evolved, and that, moreover, consisted almost exclusively of carbonic anhydride. It is therefore evident that marsh-gas is formed from the solid constituents, although albuminous bodies, fat, and starch need not necessarily be concerned in its production. For the artificial production of the marsh-gas fermentation of cellulose, a 1 per cent. neutralised meat-extract solution, and some cellulose (paper pulp), were sterilised and then infected with paunch contents. After 3—8 days, a plentiful development of gas had occurred, which consisted almost solely of carbonic anhydride and methane. The relation between the two gases at the beginning was 7·2 to 1, at the end of the fermentation 3·4 to 1. In a quantitative determination, the author found 38 per cent. of the cellulose appeared as gas. The non-gaseous products were volatile fatty acids, acetic and butyric, with a small quantity of aldehyde.

If these results be compared with the after-fermentation products of the paunch contents, a strict analogy will be seen to exist between the gases of these two fermentations:—

	From the paunch contents of ox.	From the paunch contents of goat.	From the paper pulp fermentation.
CO <sub>2</sub> }			
SH <sub>2</sub> }			
H .....	0·07	—	—
CH <sub>4</sub> .....	23·27	24·53	23·01
N .....	1·31	0·15	—

The non-gaseous products of the paunch fermentation consists of a small quantity of formic and propionic acids and aldehyde, large quantities of acetic and normal butyric acids, and an acid having the composition of butyric acid, but none of the characteristic properties of either the normal or iso-acid (formic, propionic, and normal butyric acids were not found in the artificial fermentation). As such large quantities of fatty acids were formed, it was necessary to see to what extent they existed preformed in the food (hay): for this purpose

1 lb. of hay was digested with boiling water for one hour, but from this only 0.6 gram of fatty acids was obtained. The author concludes, therefore, that cellulose is the body which, for the most part, gives rise to carbonic anhydride, methane, and fatty acids through the action of bacteria. The gaseous and non-gaseous fermentation products of the cæcum and colon of the horse agree with the marsh-gas fermentation products. This is true also for the big intestine of the ruminants, only the amount of acid formed is not so large. More is formed after feeding with corn than after feeding with hay.

Taking into consideration the fact that the putrefaction of albuminous bodies can proceed without any essential formation of methane, and the large quantity of this gas found in the case of ruminants, the author concludes that the marsh-gas fermentation of cellulose is the only means by which cellulose is rendered soluble in the intestines of ruminants.

With nourishing media of certain composition, a fermentation and solution of cellulose can occur without the formation of any methane, hydrogen and carbonic anhydride only being produced; the other products, however, remain unaltered. The fermentation that takes place in the horse's stomach is similar to this, and is considered by the author to be a hydrogen fermentation of cellulose.

J. P. L.

**Odour and Poisonous Effects of the Products of the Fermentation produced by the Comma Bacillus.** By W. NICATI and RIETSCH (*Compt. rend.*, **99**, 928—929).—Pure cultivations of the comma bacillus have a characteristic ethereal odour, quite different from that of putrid substances. This is the odour of the intestinal matter of cholera patients in the early stages, especially if it is kept in a moist atmosphere at 25—35° for 24 hours. If pure cultivations of this bacillus in Koch's gelatin or in beef tea, *after at least eight days*, are freed from bacilli by being passed through a Pasteur's filter, and the clear liquid is injected into the circulatory system of dogs, choleraic symptoms of varying degrees of violence are produced. The same liquid when injected under the skin has no effect. *Recent* cultivations are also absolutely inactive.

C. H. B.

**Value of Disinfectants in Chicken-cholera.** By COHN (*Compt. rend.*, **99**, 934—935).—The intestinal matter and some very vascular tissues from poultry which had died from chicken-cholera were treated with copper sulphate, zinc chloride, chloride of lime, or borax, in different proportions, and various animals were inoculated with the products. Copper sulphate and zinc chloride are much more efficient than borax or chloride of lime, but their complete efficiency depends entirely on their being mixed intimately in considerable quantity with the infected matter, and left in contact with it for some time.

C. H. B.

## Chemistry of Vegetable Physiology and Agriculture.

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**The Ammoniacal Ferment.** By A. LADUREAU (*Compt. rend.*, 99, 877—878).—The ferment which converts carbamide into ammonium carbonate exists in considerable quantity in the soil, in the air, in rain, and in many subterranean waters. It acts as readily in a vacuum or under a pressure of 3 atmos. as under the normal pressure, and equally well in presence of air, oxygen, nitrogen, hydrogen, carbonic anhydride, or nitrous oxide. Anæsthetics, with the exception of chloroform, which retards fermentation, exert little or no action on it, and fermentation is only prevented by somewhat high proportions of the ordinary antiseptics.

This ferment converts all the carbamide produced by the animal kingdom into ammoniacal salts, and thus places many millions of kilograms of these salts daily at the disposal of plants. C. H. B.

**Peptonic Fermentation.** By V. MARCANO (*Compt. rend.*, 99, 811—813).—If a few drops of the sap of the American aloë are allowed to fall on some chopped meat covered with water, and the whole is kept at 35—40°, active fermentation immediately commences, with evolution of inodorous gases, and after about 36 hours the fibrin completely disappears, and is converted into peptone, together with some pepsin and small quantities of ethyl alcohol and lactic acid. This fermentation is also produced by many other saps and by the juices of many fruits. It is due to a *mucor*, which can be submitted to several successive cultivations without losing its activity. C. H. B.

**Germination of Linseed and Sweet Almonds.** By A. JORISSEN (*Ann. Agronomiques*, 10, 468—475).—The author has studied the influence of germination and growth on the development of hydrocyanic acid in the flax and sweet almond. 20 grams of crushed flax seed do not yield more than 2 mgrms. of hydrocyanic acid, but after some days of germination 14 mgrms. are obtained from the same quantity. The young plants, however, yield only traces on plunging them suddenly into boiling water and distilling the whole, so that probably a glucoside similar to amygdalin or laurocerasin is formed during germination, and splits up under suitable conditions into hydrocyanic acid, glucose, and benzaldehyde.

Sweet almonds contain mere traces of amygdalin, but when they are kept moist and allowed to germinate in darkness for some weeks, a well-marked odour of benzaldehyde is produced, and hydrocyanic acid can be obtained in recognisable quantity (2 mgrms.) from a single seedling. The amygdalin is concentrated in the radicle and gemmule, the cotyledons containing very little. By suitable treatment, the three substances, benzaldehyde, glucose, and hydrocyanic acid, were isolated from 15 germinated almonds. The author believes

amygdalin and similar glucosides to be decomposition-products of the albuminoids of the seeds.

J. M. H. M.

### **Chlorophyll in the Living Cell and Assimilation of Carbon.**

By J. REINKE (*Bied. Centr.*, 1884, 692—696).—The reduction of carbonic anhydride in plants is a function of light and of the chlorophyll, but to properly understand the process it must be studied in the living plant. The author did so, using the leaves of *Phanerogama*, and observing their absorption-spectra, he found that of the ordinary chlorophyll solution different from that obtained from the living leaves, the latter agreeing amongst themselves. He believes that chlorophyll experiences some chemical change when it is dissolved. The solution of the fresh leaves shows no fluorescence, but the ordinary solution shows a fine red fluorescence, due probably to the disaggregation of the substance, which the author believes to exist in a fixed state. The spectroscopic examination of light reflected from the leaves is of interest, the extreme red to line B being very brilliant, the space between C and E moderately so, the dark blue and green being weak. The author agrees with Lommel that the maximum of carbon reduction coincides with the maximum of absorption of the chlorophyll spectrum, that the molecules have a vibratory motion, and when they meet a ray of light in unison with them they assimilate its life-giving force, and chemical changes result. The author found a theory on his observations that the atomic group on which depends the reduction have an oscillation rate of 440—450 billions per second, and are set in motion by rays of light of similar rate, whilst they remain unaffected by rays of higher or lower refrangibility.

J. F.

**Presence of Amylase in Leaves.** By L. BRASSE (*Compt. rend.*, 99, 878—879).—The author has found amylase in all leaves which he has examined, including those of the potato, dahlia, maize, beet-root, tobacco, castor-oil plant, &c. The amylase can be extracted by Dubrunfaut's method. The leaves are bruised in a mortar, digested with cold water for 24 hours, squeezed, and the solution mixed with one and a half times its volume of alcohol of 90—93°, and filtered. The filtrate is again mixed with the same proportion of alcohol, and the precipitate collected on a filter and washed two or three times with a small quantity of alcohol of 63°. This precipitate contains the amylase.

To detect the amylase, 0.5 gram of starch, 20 c.c. of water, and 10 c.c. of an aqueous solution of amylase of such strength that 10 c.c. corresponds with 10 grams of fresh leaves, are placed in a small flask and kept at 63° in a water-bath for some time. Similar flasks containing a solution of amylase alone are treated in the same way, and the reducing sugar is estimated by difference. Each flask is closed with a cork, and contains from 8 to 10 drops of chloroform. In every case, the starch is converted into reducing sugar and dextrin, but no microbes are developed.

C. H. B.

**Chemical Composition of Hazel Pollen.** By A. v. PLANTA (*Landw. Versuchs-Stat.*, 31, 97—114).—Hazel pollen separated from



the dried catkins by means of a fine sieve is a very fine pale-yellow powder, which keeps for any length of time when perfectly dry. It consists of very small nodules (from 0.026 to 0.0337 mm. in diameter), of triangular and oval shape, each nodule having three openings for the pollen tubes, and being surrounded by two membranous coats closely united together. The contents of the nodules consist chiefly of protoplasm and oil with a little starch.

Hazel pollen contains 9.19 per cent. of water, of which nearly half is given up on drying over sulphuric acid. The quantity of nitrogen was found to vary in two samples from 4.70 to 5.50 per cent., and the ash amounted to 3.81 per cent. By employing the usual factor for the conversion of nitrogen into proteids, the nitrogen-free substances were inferred to amount to about 64.3 per cent. of the dried pollen.

The impossibility of mechanically breaking up the pollen nodules, and the difficulty of thorough extraction of their substance by liquid agents, rendered the estimation of the separate organic constituents no easy task, and some of them could only be determined qualitatively. Of nitrogenous bodies, globulins, peptones, hypoxanthine, and amido-compounds were definitely traced, the latter yielding about one-twelfth of the total nitrogen. Cane-sugar was found in considerable quantity, amounting to about 14.7 per cent. of the dry pollen, and starch was estimated at 5.26 per cent. A yellow colouring matter containing no nitrogen was found in quantity amounting to 2.06 per cent., and consisting probably of two distinct bodies. Cuticula was put down at 3.02, and wax at 3.67 per cent., the latter consisting probably of myricyl palmitate. Fatty acids amounted to 4.2 per cent. The presence of cholesterin was also noted, and a resinous substance of bitter taste was found in quantity amounting to 8.4 per cent. J. K. C.

**Ash of Strawberries.** By J. M. H. MUNRO (*Chem. News*, 50, 227).—Strawberries grown in a field in Kent contained—water 89.30 per cent., organic matter 10.27, ash 0.43. The composition of the ash was as follows:—

Sand and insoluble matter 6.61 per cent., calcium phosphate 23.91, containing 11.70 per cent. of phosphoric anhydride; magnesium phosphate, trace; potassium carbonate 60.77, containing 41.40 per cent. of potassium oxide; magnesia 2.93, soda 1.29, sulphuric anhydride 3.88, undetermined 0.61.

The figures seem to show that in the strawberry the whole of the potash exists in combination with organic acid, and the whole of the phosphorus as calcium phosphate. Strawberry growers assert that plants forced in pots with the aid of guano or very rich soil have many blossoms, but they do not all set, or if they do the fruit is inferior in size and quality to the smaller quantity produced in poorer soil. It seems probable that a special manure containing a fair proportion of potash would produce good results. J. T.

**Ensilage and Acidification of Green Fodder.** By J. KÖNIG and others (*Bied. Centr.*, 1884, 677—680).—Green maize, previously cut fine, was stored in a silo 5 metres deep, with cemented walls. At the time of storing, three casks were filled with the same fodder, and

they were compared at intervals with samples drawn from the silo. Unfortunately one of the walls became damaged, and water leaked in, but the experiment was sufficiently successful to convince the author that the loss of dry substance in green maize stored in silos which are air and damp-proof does not exceed 10 per cent. E. Lecouteux records experiments made to ascertain whether the maize should be cut (chopped) or stored whole. He recommends chopping, as by that means the portions lie closer together, and facilitate fermentation; the fine and coarse portions of the fodder are more evenly mixed, so that cattle cannot pick out the choice morsels. Stutzer has tried the acidification of green clover. He found that the digestible albuminoids were diminished by one-half in the operation, the comparison being made by artificial digestion. A feeding experiment was made with ensilage-grass by Insinger, in Holland. Out of a lot of 32 cows, 4 were fed on the ensilage; the others on hay. The period of lactation was longer with the 4 cows; the creamometer-indication lower; butter percentage higher, 54 litres of their milk producing 2.5 kilos. of butter, the same quantity of milk from the others giving 2 kilos. only. The colour of the butter was rather dark. J. F.

**Removal of the Bitter Principle from Lupines.** By E. WILDT (*Bied. Centr.*, 1884, 675—677).—Experience has shown that exposure to the atmosphere sweetens lupines, and removes their poisonous qualities. As this cannot be done even by strong heat, the author thought that the change was caused by a process of oxidation, and that it could be greatly accelerated. He placed the seeds in dilute hydrochloric acid, and then treated them with a solution of calcium chloride; they were then well washed with clean water. By this process the bitterness was quite removed, and probably also their poisonous qualities (but this has yet to be proved on a large scale); the loss of nutritive matter was small. The author thinks that lupines prepared in this way will be found to be a good and cheap fodder. Cattle, sheep, and swine eat them with more or less readiness, but the reports by cattle-feeders as to the results are not unanimous; some say they are not a fattening food, and that draught oxen and horses grow lean on them, owing probably to the excess of nitrogenous constituents. J. F.

**Ensilage of Frozen Potatoes.** By J. FITTBOGEN and O. FOERSTER (*Bied. Centr.*, 1884, 681—683).—In the autumn of 1881, a sudden and severe frost damaged large quantities of potatoes throughout Germany. The quantity was so large that the distilleries were not able to use them, and they had to be stored in silos. The authors embraced the opportunity of examining them at different times—at time of storage and after 50, 76, and 140 days. At the last examination, the loss of crude protein was 33.7, and of crude fat 83.3 per cent. Cattle and swine eat freely of them, but sheep did not take them. The authors do not recommend the proceeding unless nothing else can be done with the tubers. J. F.

**Cultivation of Sugar Beet.** By P. P. DEHÉRAIN (*Compt. rend.*, 99, 920—922).—It has been observed in many cases that the use of

a manure rich in nitrogen increases the proportion of this element in the beet, but diminishes the proportion of sugar. The author finds, however, that by using properly selected seed, *e.g.*, the cultivated variety of Messrs. Vilmorin, the proportion of sugar is not diminished by even a highly nitrogenous farmyard manure, whilst the total yield of roots per hectare is considerably increased, especially if the manure is mixed with sodium nitrate.

One of the causes which diminish the proportion of sugar in the beet is the late sprouting of young leaves, the development of which uses up the sugar previously formed in the root. If, however, the last month of vegetation is dry, this growth of new leaves does not take place, and the value of the roots is increased. C. H. B.

**Hop Culture in Peat Soils.** By M. FLEISCHER (*Bied. Centr.*, 1884, 716).—The author gives analyses of the soil of a hop plantation in East Prussia, established in a boggy situation. The constituents indicate great suitability for the culture in question, but owing to the lightness and porosity of the soil, the frost penetrates it easily in winter, and injures the roots of the plants. J. F.

**On Rotations.** By P. P. DEHÉRAIN (*Ann. Agronomiques*, 10, 433—457).—The author reviews the leading systems of rotation practised in the north of France and in Germany, and suggests a modification of the prevailing French rotation, founded on the experiments which have been for some years carried on at the Agricultural Station of Grignon (Paris).

The increasing importance of stock-raising, and the development of beet sugar refineries and spirit distilleries, have brought about the substitution of a crop of sugar beet for the bare fallow formerly customary throughout large districts of France and Germany. This beet crop takes the place of the English turnip crop at the head of the rotation, which runs thus:—beet, corn, seeds, corn. All the farmyard manure intended for the rotation is given to the beet crop, and this has the effect of producing a heavy crop of large roots poor in sugar. The French refiners pay for the roots according to the gross weight, and not on the percentage of sugar; hence the farmers have gone on applying larger and larger dressings of dung, and supplementing these by applications of nitrate of soda and sulphate of ammonia, with the view of getting heavier and heavier crops. The natural result has followed, that the French sugar industry is in a languishing and critical state. In Germany, on the other hand, where the refiners pay for the roots according to their richness in sugar, the industry has undergone an immense development. The German farmers, in order to secure roots of good quality, commence the rotation with a wheat crop manured with farmyard manure, and take the sugar beet crop the year after. To do this successfully they are obliged to grow a variety of wheat (Sheriff Square Head) which will stand the heavy manuring without running too much to straw, and becoming laid. The Sheriff Square Head wheat, however, produces grain of inferior quality and low market value, and on this ground the author does not recommend the German system. Neither

does he think well of putting potatoes at the head of the rotation instead of sugar beet, because potatoes derive little or no benefit from heavy dressings of farmyard manure, and it is a mistake to suppose that the subsequent crops of the rotation utilise anything like the full value of the manure unused by the potato crop.

From the results of several years' experiments at Grignon, it is inferred that maize cut green for fodder would do well to begin a rotation over districts of similar soil and climate. During the early stage of growth, the ground can easily be kept free from weeds, and during the later stages the growth is so luxuriant that weeds are stifled. Large applications of farmyard manure always produce a very heavy increase in the maize crop, and are more efficacious than any other manures which have been tried. The maize can be made into ensilage, which the author thinks the better plan, or can be grown in successive portions, and cut as required for feeding. Very heavy crops can be obtained (70,000—100,000 kilos. per hectare at Grignon, with 30,000 kilos. farmyard manure per hectare), and the succeeding wheat crop is decidedly better than when it follows sugar beet. Moreover, the maize being cut in September, more time is allowed for preparing the ground for the autumn sowing of wheat than when beet is grown, which is pulled in October. The wheat crop should receive 5,000—10,000 kilos. farmyard manure, and 200 kilos. nitrate of soda. At Grignon, sulphate of ammonia cannot be substituted for the nitrate of soda without injury, but on other soils (Rothamsted, for example) it is found to answer well. The sugar beet crop is to be taken after the wheat, and is to be manured with 20,000 kilos. farmyard manure, 200 kilos. nitrate of soda, and also superphosphate on soils where it is found to produce an increase, which is not the case at Grignon. In the fourth year, the ground carries oats sown with seeds, and manured with 5,000—10,000 kilos. farmyard manure and 200 kilos. nitrate of soda; fifth year, clover; sixth year, wheat or oats; and seventh year, potatoes; all without manure. If the oats in the fourth year are sown with sainfoin instead of clover, the ground may be left in sainfoin two or three years before taking the next wheat crop.

J. M. H. M.

**Manuring Experiments.** By G. DRECHSLER (*Bied. Centr.*, 1884, 664—670).—These experiments were made in Hanover in 1880, with very careful precautions against error. Each manuring was repeated at least three times, and each manured plot was surrounded by at least four unmanured. Those experiments alone were considered to be quite successful in which the yields of the unmanured plots were very close to each other, and the results of the three trials of the manured plot were nearly concordant. Under such conditions, a number of landowners undertook to carry out experiments to ascertain how Chili saltpetre operates on potatoes as compared with the potash salt, and to compare the action of kainite on potatoes, barley, and oats with a compound manure containing kainite, sulphate of magnesia, and common salt.

The potash gave unexpectedly low results in all experiments, being lower in heavy, well-tilled lands than on light soils; the increase in

almost all cases consisted in large tubers; Chili saltpetre and phosphates, with few exceptions, yielded very good results. In the trials with the compound manure, some were unsuccessful, because of a dry season, but in the completed experiments the results were more in favour of potash than of kainite, whilst the compound manure came out very badly.

J. F.

**Notes on Manuring.** By G. DRECHSLER (*Bied. Centr.*, 1884, 658—664).—The author has made many experiments himself, and has studied the results of those made by others, with a view of modifying the theories of Liebig, on which most of the modern practices of manuring are founded, the rule being that manuring is to be regulated according to the requirements, or rather the constituents, of the crop to follow, allowing for the disposable nutritious matters contained in the soil; and as the knowledge of this cannot generally be obtained in advance, experience only must be relied on, namely, if the use of a manure increases the yield, it is concluded that there was a deficiency in the soil; if the manure is inoperative, the soil is supposed to contain a surplus.

From his experience, the author formulates new theories of manuring. (1.) The nutriment in the soil and that contained in manures are of different natures, and by reason of the difference in their solubilities, combinations, &c., they operate differently on the plant. (2.) The power of different plants to assimilate nutriment from manures varies, and differs sometimes in the same class of plants. (3.) He divides the process of manuring into two parts—the art of supplying to the soil the matters deficient, which he calls field manuring; and that of supplying for the plant the nutriment it is known to require; this he names plant manuring. These theories admitted, the question of manuring becomes a consideration not of the soil, but of the plant, and the first thing to be learned is the requirements of the crop which must be supplied in the manure, what modification of such requirements is found on growing it in certain soils, and what is the best and cheapest manner to supply the necessary matter in the manures. The author commends Wagner for carrying out experiments in this direction so carefully by means of pot culture, but recommends further field experiments.

J. F.

**Manuring Experiments with Chili Saltpetre.** By L. KOCH (*Bied. Centr.*, 1884, 673).—Experiments were made with plots of wheat and rye as to whether larger or smaller quantities of sodium nitrate gave the best results.  $1\frac{1}{2}$  kilos. to about one-fourth of a square metre gave a better crop than  $2\frac{1}{2}$  kilos., but the summer was dry and hot, and the harvest time wet, so that the results of the experiments are of little value.

J. F.

**Preservation of Ammonia in Stable Manure.** By TROSCHKE (*Bied. Centr.*, 1884, 670—672).—The addition of gypsum to stable manure, particularly in warm stalls, is known to cause decomposition of the ammonia and evolution of sulphuretted hydrogen. The author

tried kainite as a substitute, with the following result for three months' contact in warm weather:—

Loss.	With kainite.	Gypsum.
In dry substance .....	20 per cent.	31 per cent.
Nitrogen.....	10 „	32 „

He therefore thinks the employment of gypsum unadvisable. Further experiments were made as to the power of Stassfurt salts to form combinations with ammonia. 100 grams of each salt were mixed with different percentages of ammonia, and the number of grams combined with the salt after 24 hours is given.

100 grams.	20 per cent.	50 per cent.	80 per cent. mixture.
Magnesium chloride .....	6·2	11·5	12·6
Magnesium sulphate .....	5·5	6·9	7·0
Gypsum .....	5·0	17·8	19·8
Kainite.....	3·2	6·4	7·3
Carnallite.....	4·8	9·0	9·4
Krugite.....	3·0	7·8	10·5
Kieserite .....	4·5	10·5	11·1

In order to learn the power of the salts to absorb ammonia in the gaseous form, portions of each were exposed in large flasks to the vapour of ammonium carbonate for one, two, and three days, with the following results:—

100 grams of	Combined with grams $\text{NH}_3$ in—		
	1 day.	2 days.	3 days.
Magnesium chloride ..	6·1	11·3	12·0
Magnesium sulphate ..	5·1	6·4	6·9
Gypsum .....	5·0	9·9	12·8
Kainite.....	2·9	4·2	6·2
Carnallite.....	4·1	8·5	9·0
Krugite.....	1·9	3·7	4·5
Kieserite .....	4·1	8·2	10·5

The substances should be used in a very fine state of division.

J. F.

**Experiments on the Nitrogen of Peat.** By P. REDER (*Bied. Centr.*, 1884, 652, 655).—The author wished to ascertain the effect produced on the nitrogen contained in peat by the addition of certain matters thereto. The original sample contained a total of 3·225 percent., of which 0·109 was in the form of ammonia, 0·053 of nitric acid, and 3·154 in inorganic combination. One portion of the peat was left with free access of air, another without air; to neither of them was any addition made. To other seven samples were added calcium carbonate, freshly burnt lime, gypsum, magnesia, potassium carbonate, sulphuric acid, quartz sand. The samples were left for 12 months and then examined. All showed a loss of nitrogen, with the exception of that treated with sulphuric acid, and the author attributes the increase of nitrogen in that sample to absorption from the air of the laboratory. A feature

common to all was an increase in the amount of nitrogen existing as nitric acid, and a diminution of its other combinations. J. F.

**Effects of Fresh Stable Manure on Potatoes.** By GAGNAIRE (*Bied. Centr.*, 1884, 700).—It has been found by the author as well as by other observers that the application of fresh manure at the time of planting caused a considerably increased yield of potatoes, but that the plants were more liable to disease. A field so manured compared with another which had received the manure the previous autumn showed an increase of one-eighth in the yield, but when the tubers were stored a great part of them became bad in a few weeks.

J. F.

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## Analytical Chemistry.

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**Modification of Dumas' Method for the Estimation of Nitrogen.** By G. S. JOHNSON (*Chem. News*, 50, 191).—The modification suggested is as follows:—A long combustion tube is drawn out at the front end, so as to form a delivery-tube; in the front, reduced metallic copper is packed, and behind this copper oxide, whilst quite at the back a platinum boat (4 to 5 inches long) is inserted. The substance to be burnt is put in the front half of this boat, the back part being filled with pure powdered potassium chlorate; a cork with a piece of glass tube passing through closes the back end of the combustion tube. When in operation, a stream of carbonic anhydride is sent through the tube, and is continued steadily throughout the combustion. After 10 minutes, the whole front part of the tube is heated, and as soon as all free nitrogen is driven out of the tube, the trough, tube with caustic potash, &c., are adjusted for the reception of the nitrogen from the substance under examination, which is first heated without fusing the potassium chlorate. When the evolution of nitrogen ceases from this destructive distillation, the heating is extended to the chlorate, and the operation is complete with the cessation of the production of nitrogen. The advantages claimed are that the air is driven from the copper oxide more rapidly by a stream of carbonic anhydride at a red heat than it is at the ordinary temperature. When platinum, gold, or silver salts are burnt, the metal remains in the boat with the potassium chloride, and after washing may be weighed, whilst observing the ratio that the nitrogen obtained in the first part of the combustion (the distillate) bears to that obtained from the combustion of the residue (after heating the chlorate) may be of use in determining the constitution of the nitrogenous compounds. D. A. L.

**Method of Testing for Iodine in Presence of Large Quantities of Bromine.** By P. S. BRITO (*Chem. News*, 50, 210).—When bromine and iodine are liberated by chlorine, and in the usual manner carried down by chloroform, the bromine masks the colour



of the iodine if it is in excess. The author finds that the addition of a few crystals of ferrous sulphate removes the brown bromine coloration, and renders visible the minutest trace of iodine dissolved by the chloroform. By this means a trace of iodine was detected in "pure" potassium bromide. D. A. L.

**Rapid Estimation of Fixed Ammonia.** By J. W. PRATT (*Chem. News*, 50, 192).—The present method is well suited for testing "gas-water" and "bone-liquor." Free ammonia is determined as usual by direct titration. For the fixed ammonia, about 25 c.c. of the liquid is evaporated to dryness with 25 c.c. decinormal sodium carbonate, ignited to get rid of any organic matter, redissolved in water, and titrated. The amount of fixed ammonia is easily calculated from the quantity of sodium carbonate consumed. Allowance must be made for, or the method must be modified, if the liquid has a non-volatile alkalinity. D. A. L.

**Electrolytic Estimations.** By A. CLASSEN (*Ber.*, 17, 2351—2359).—In a recent paper (*Abstr.*, 1884, 1426) Wieland has criticised adversely the methods for the electrolytic estimation and separation of iron, manganese, and aluminium described by the author (*Abstr.*, 1881, 1081; 1882, 896). Numerous fresh results are now given, confirming the accuracy of these methods, and it is pointed out that Wieland's failure to obtain good results is entirely due to his neglect of precautions stated to be necessary in the author's earlier papers. A. J. G.

**Quantitative Analysis by Electrolysis.** By A. CLASSEN (*Ber.*, 17, 2467—2485).—This is a continuation of the author's previous communications (*Abstr.*, 1881, 1081, and 1882, 896) on this subject.

The author advises the use either of one of the ordinary batteries (Bunsen, Leclanché, Daniell, &c.), or of a small Siemens dynamometer. By the help of an arrangement to regulate the rate of revolution, and the introduction of a rheostat into the circuit to further regulate the current, the author has obtained very satisfactory results with a Siemens machine. Thermoelectric batteries were not found to work satisfactorily. Two Bunsen cells are sufficient for most purposes, and are connected either in series, or as a pair, according as the metal in question is easily deposited or not. The author estimates the strength of the current by the number of c.c. of gas generated per minute by the decomposition of acidified water.

*Estimation of Copper and Cadmium.*—These metals are reduced from solutions of their ammonio-oxalates by a weak current (two Bunsens joined as a pair). If a stronger current is used, they are deposited in a spongy condition. They may thus be separated from other metals requiring a stronger current for their electrolysis. To separate copper from iron, excess of ammonium oxalate is added to the mixed solution, and the copper then deposited in the cold by a current from two Bunsen cells arranged as a pair: in about 10 hours all the copper is deposited. More ammonium oxalate is then added, the Bunsen cells arranged in series, and the iron electrolysed. The

separation of copper from nickel, from cobalt, and from chromium, is effected in a similar manner. The separation of copper from manganese can be effected in the same way, but the current must be kept as constant as possible, as otherwise traces of manganese may be deposited on the positive pole or of manganic dioxide on the negative. In separating copper from zinc by the electrolysis of their ammonio-oxalates, the action must be stopped as soon as all the copper is deposited. The separation is more easily effected if the solution to be electrolysed is acidified with sulphuric acid. Copper cannot be separated from antimony, arsenic, mercury, bismuth, or cadmium by the electrolysis of their ammonio-oxalates. It may, however, be easily separated from cadmium if the solution is acidified with nitric acid and electrolysed. In these reactions, potassium ferrocyanide is the best means of testing whether all the copper has been deposited, as the ammonium test loses much of its delicacy in presence of oxalic acid.

*Estimation of Antimony.*—The method previously proposed for the estimation of antimony by electrolysis in the presence of excess of ammonium sulphide (Abstr., 1881, 1081) has several drawbacks. The smell produced is very unpleasant, and if the ammonium sulphide contains polysulphides, or free ammonia, unsatisfactory results are obtained. Better results are obtained with sodium or potassium sulphide, but even here care must be taken that no polysulphide is present, and that the sulphide employed is free from iron and alumina. The electrolysis must be conducted in the cold, and a current yielding 2 to 3 c.c. of electrolytic gas per hour employed. The quantity of antimony in solution must not exceed 0.2 gram.

*Estimation of Tin.*—Tin is best deposited from solutions of its ammonio-sulphide. If dilute sodium or potassium sulphide is employed, the precipitation is only partial, and the author believes that a complete separation of antimony from tin might be effected by using concentrated sodium sulphide.

*Estimation of Platinum (Potassium, Ammonium).*—The deposition is effected by the current from a single Bunsen cell. The solution employed may be acidified either with hydrochloric or sulphuric acid, and ammonium or potassium oxalate added: the solution should be slightly warmed. The author contends that the estimation of potassium, ammonium, and nitrogen, by means of the electrolytic deposition of platinum from their platinochlorides, is more exact and expeditious than the ordinary gravimetric method.

*Estimation of Iron.*—In separating iron and cobalt, both metals are deposited by electrolysis of the double oxalates, and the total weight found. This deposit is then dissolved in dilute sulphuric acid, and the iron titrated with permanganate, or it may be dissolved in hydrochloric acid, and the iron then oxidised with hydrogen peroxide and titrated with stannous chloride. The cobalt is estimated by difference. The same method may be employed for separating iron and nickel, but the reduced metals require strong hydrochloric acid for their solution. This method of estimation may also be employed with a mixture of iron and zinc, provided that the quantity of zinc present is less than one-third that of the iron; if the zinc exceeds this pro-

portion, the results are unsatisfactory. In a solution containing iron and uranium, the iron may be deposited by means of a current from two Bunsen cells in series, whilst if a large excess of oxalate is used, the uranium is retained in solution.

*Estimation of Zinc.*—Zinc is separated from chromium or from uranium by electrolysing the oxalates by means of a current yielding 10 c.c. electrolytic gas per minute; the zinc is deposited and the chromium or uranium remains in solution.

In the electrolysis of the mixed oxalates of chromium and uranium, the latter metal is deposited as hydroxide, whilst the former remains in solution. Cobalt in the presence of chromium or manganese, is estimated in a manner similar to that described above for the estimation of zinc.  
L. T. T.

**Decomposition and Analysis of Slags.** By M. W. ILES (*Chem. News*, 50, 194—196).—The following methods are those which are in daily use, and are recommended by the author for the analysis of ores and slags connected with the lead-silver industry. To sample and prepare for analysis: slag is allowed to run upon the end of a steel bar, or the bar is dipped into a pot of freshly drawn slag, then plunged into cold water, and the slag dried, and finely powdered. This method of rapid cooling does not materially affect the chemical composition of the slag, but renders it readily decomposable by hydrochloric acid. The author finds that all slags containing from 30 to 42 per cent. of silica are entirely decomposed in this manner, and, moreover, he believes that the method would answer equally well with iron slags. The silica is determined much in the ordinary way, care being taken to thoroughly oxidise the iron before evaporation. For iron, about 0.5 gram of prepared slag is decomposed with hydrochloric acid, diluted, reduced with zinc, diluted to 500 c.c., about 25 c.c. of concentrated sulphuric acid added, and the iron titrated with  $\frac{N}{50}$  permanganate. For manganese, the finely powdered slag is decomposed with hydrochloric acid with the addition of a few drops of nitric acid, the solution is boiled, and sulphuric acid is added until all the hydrochloric and nitric acids are replaced by it. This solution is diluted to 150 c.c., boiled, the iron precipitated by excess of zinc oxide emulsion, and is filtered off along with the silica. The filtrate is made up to 500 c.c., and the manganese determined by titration with permanganate. For calcium, the filtrate from the silica determination is heated, made alkaline with ammonia, and oxalic acid added to dissolve the iron; the calcium oxalate is collected, washed, dissolved in hydrochloric acid, filtered, diluted and decomposed by boiling with a large quantity of sulphuric acid; the oxalic acid is then titrated with permanganate. When greater accuracy is desired, the iron and alumina are removed as basic acetates, the manganese by bromine-water, the zinc by hydrogen sulphide, and the filtrate is treated in the usual manner. For zinc a gram of substance is digested with a mixture of 10 c.c. hydrochloric, 5 grams nitric, and 5 grams sulphuric acid (all concentrated), until thick fumes of the last-named acid appear, the mass when cool is diluted to 150 c.c., filtered and washed with hot

water. The solution is treated with 2 c.c. hydrochloric acid, saturated with hydrogen sulphide, and the precipitate is filtered and washed. The liquid is boiled and oxidised with potassium chlorate, the iron and alumina are then precipitated with a large excess of ammonia, and filtered off, the filtrate is acidified with hydrochloric acid, made up to half a litre, and the zinc titrated with standard ferrocyanide, using uranium acetate as indicator. Manganese, nickel, and cobalt interfere with this reaction, and must be removed before titration, also when ammonium chloride is present, a correction must be made. *Lead* is best determined in the dry way; if, however, *all* the lead can be got into solution as nitrate, the following method is accurate:—Add zinc oxide emulsion to the solution and titrate in the cold with decinormal permanganate to a slight rose tint, warm, and add permanganate until the second tint is observed. *Sulphur* is estimated by fusing the substance with caustic potash, and, after removal of the iron, oxidising with bromine-water, and finally precipitating as a barium sulphate. For *arsenic*, Pearce's method is the best, whilst Volhard's volumetric silver method, when it can be used, proves an excellent one. Other substances are estimated by the ordinary methods.

D. A. L.

**Remarks on the Analysis of Soils.** By W. KNOP (*Landw. Versuchs-Stat.*, 31, 155—158).—To estimate the quantity of lime and magnesia present as carbonates and in combination with humic acid, the author recommends mixing the soil with potassium chlorate and heating until oxygen begins to be evolved. If the soil is very rich in humus, it must be first mixed with a sufficient quantity of pure quartz sand, in order to prevent the action from being too violent. This method was tried with a very rich soil from Banat, and yielded perfectly satisfactory results. The sample contained 27 per cent. water, 23 per cent. humus, and the remainder was composed almost entirely of quartz and silicates of alumina.

J. K. C.

**Separation of Zinc from Nickel.** By T. MOORE (*Chem. News*, 50, 151).—The author recommends the following process for the separation of zinc from nickel as effectual and easy. Expel the excess of acid by evaporation from the solution containing the two metals, dissolve the residue in 20—25 c.c. of water, and precipitate with excess of ammonium sulphide. Dissolve the precipitate by heating it with potassium cyanide, make up the solution to 250 c.c., add a few c.c. of sodium acetate solution, acidify with acetic acid, and heat to boiling. After a few hours wash the zinc sulphide with water containing a small quantity of sodium acetate and hydrogen sulphide, and finally convert it into oxide in the usual manner. To estimate the nickel:—Evaporate the filtrate and washings to dryness with aqua regia, dissolve the residue in water, and precipitate with potassium hydroxide and bromine. Redissolve the precipitate in dilute sulphuric acid, adding ammonia, and precipitate the metal by electrolysis.

D. A. L.

**New Method for Separating Copper from Cadmium.** By P. GUCCI (*Ber.*, 17, 2659—2660).—After bismuth has been separated in

the usual way by the addition of ammonia, hydrochloric, nitric, or sulphuric acid is added in sufficient quantity to redissolve the hydroxides of copper and cadmium, and then the copper is precipitated by a 10 per cent. solution of ammonium benzoate added in slight excess. The filtrate is tested for cadmium by the addition of ammonia and ammonium sulphide. This separation is very complete, and may be used with advantage in quantitative analysis.

A. K. M.

**Determination of Iron and Chromium in Alloys.** By H. PETERSON (*Chem. News*, 50, 210).—The author's method is based on the fact that chromium sulphate in a sulphuric acid solution is oxidised into chromic acid by boiling with permanganate. Half a gram of finely divided alloy is dissolved by boiling with 35 c.c. of dilute sulphuric acid; if any hydrocarbons are dissolved they are oxidised with permanganate, and the ferric salt thus formed is reduced with zinc, the liquid diluted to 1 litre, and the iron titrated with permanganate. When the titration is complete, the liquid is boiled, while permanganate is dropped in until there is a plentiful precipitate of manganic oxide, which is filtered off and well washed with hot water. When cool, the chromic acid is determined in the liquid by adding ferrous ammonium sulphate in excess and titrating back. If the amount of chromium only is required, it is neither necessary to destroy the hydrocarbons nor to dilute to such an extent.

D. A. L.

**Estimation of Ammonia in Potable Water.** By G. GORE (*Chem. News*, 50, 182—186).—The author has investigated this subject experimentally, and below is given an epitome of his experiments, results, and conclusions.

The water employed in the experiments was an ordinary potable water yielding, by Wanklyn and Chapman's method, 0.026 per million "free" and 0.138 per million "albuminoid" ammonia.

When 500 c.c. of this water were distilled without previous addition of sodium carbonate, the first 50 c.c. of distillate contained only a trace of ammonia; when, however, a similar quantity of this water was mixed with various ammoniacal compounds before such distillation, the first 25 c.c. always contained ammonia, as will be seen from the appended table:—

Mgrms. of NH <sub>3</sub> added.	In form of	Mgrms. NH <sub>3</sub> dis- tilled over in 25 c.c.
0.5	ammonia solution	0.11
0.05	" "	0.019
0.028	ammonium carbonate	0.019
0.04	" chloride	0.024
0.02575	" sulphate	0.0125
0.02568	" phosphate	0.0120

From the result of a special experiment, the author attributes this distillation of ammonia to the dissociation of the salts by heat. It does not take place in presence of aluminium salts, and therefore in such cases sodium carbonate must be added before distilling. It is evident from these results that the more correct way of determining

the presence of "free" or "saline" ammonia in a water is by simple distillation. The water in question evidently contained a mere trace of such ammonia, or none at all, as there were no aluminium compounds present. The 0.026 per mil. of "free" ammonia (see above) must have come from other compounds, and it is shown that the carbonate appears to act on the organic nitrogenous matter. When the distillate from the ordinary carbonate method is returned to the retort and re-distilled, it gives a slightly larger amount of "free" ammonia, and by mixing the alkaline carbonate with the sample of water 12 hours before distillation a still larger increase is obtained.

Other experiments show that distillation of a water with alkaline permanganate alone gives as large a total quantity of ammonia as when a previous distillation with sodium carbonate, or distillation with a mixture of the two is resorted to; also that the water when distilled first with potash alone, then with permanganate alone, yields more ammonia than when a mixture of the two substances is employed. Ordinary permanganate was found to contain ammonia. Caustic soda does as well as potash for rendering the permanganate alkaline. A very dilute solution of urea is not converted into ammonia by distillation with sodium carbonate, only slightly if alkaline permanganate is employed, and about one-third of it is so converted when it is distilled first with potash, then with permanganate. The residue left in the retort after completion of the ordinary ammonia estimation, evaporated to dryness and heated to redness, yields a large additional amount of ammonia. The sample of water used in these experiments had a greenish colour when viewed in depths of about a metre; this was shown to be due to vegetable matter which could be precipitated by aluminium chloride; after its removal, the water was found to contain less "albuminoid" ammonia; by this treatment, therefore, the amount of ammonia due to such vegetable matter may be approximately determined. The effect on the amount of ammonia of heating the water nearly to boiling, or of exposing it to sunlight and warmth, or of agitating it with atmospheric air previous to distillation, is seen in the following tables:—

*Effect of Heating.*

	Free ammonia (by distillation without sodium carbonate).	Albuminoid ammonia.	Total.
Not previously heated....	0.010	0.130	0.140
Heated for two hours....	0.026	0.160	0.186
„        seven hours ..	0.025	0.160	0.185

*Effect of Agitation with Air.*

Not shaken .....	0.005	0.140	0.145
Shaken for five hours....	0.005	0.195	0.200
„        ten „ ....	0.010	0.185	0.195

*Effect of Exposure to Sunshine and Warmth*

Unexposed .....	0.020	0.110	0.130
Exposed .....	0.030	0.130	0.160

In all these cases, although the water has become to a certain extent more wholesome, yet when tested by the permanganate method it appears more impure than before the change. In the last experiments, the exposure was continued until the vegetable growth which formed in the water apparently ceased to increase. The author describes a special tube for the evaporation and subsequent heating to redness of residues as mentioned above; he likewise makes special reference to the various innocuous sources of nitrogen in water.

D. A. L.

**Detection of Cyanides in the Presence of Compound Cyanides.** By W. J. TAYLOR (*Chem. News*, 50, 227).—Cyanides, when in the presence of compound cyanides, cannot well be detected by the ordinary methods. It is necessary to find a substance which, whilst freely decomposing the cyanide, will leave the ferrocyanide untouched. This condition is fulfilled by hydrogen sodium carbonate. In the detection of cyanides in the presence of compound cyanides, all that is required in qualitative analysis is to distil with an adequate volume of water and an excess of hydrogen sodium carbonate; if the preliminary examination shows the presence of mercury, a few grams of zinc must be added, as mercury cyanide is somewhat refractory, but is readily decomposed in presence of metallic zinc. J. T.

**Viscosity of Oils.** By W. P. MASON (*Chem. News*, 50, 210).—In order to obtain uniform and comparable tests with regard to the viscosity of oils, the following apparatus and methods are suggested:—A glass cylinder, 22 inches long and  $1\frac{1}{4}$  inch in diameter, is fitted to a brass bottom, one-eighth of an inch thick, in the centre of which is a hole one thirty-second of an inch in diameter, the metal being bevelled away from the outside surface of the metal a half-inch or more from the hole. Eighteen inches above the plate the cylinder is marked with a thick line (the standard head), and between the 16 and 21-inch points there are graduations every one-eighth of an inch. In using the instrument all readings are compared with distilled water at  $15.5^{\circ}$ . To determine the viscosity of an oil:—See that the temperature is normal, take sp. gr., and from it calculate what head will equal 18 inches of water (this will be inversely as the sp. gr.). Fill to and maintain this head whilst timing the flow of 100 c.c. of the oil, which when divided by the standard time will give as quotient the viscosity of the oil under examination. Such an instrument has been found to work very well. D. A. L.

**Examinations of Butter.** By H. LEFFMANN (*Chem. News*, 50, 192).—As an example of the quality of the butter supplied in Philadelphia, 20 samples, sold under various names at prices ranging from 25 to 45 cents per pound, were examined by determining the amount of alkali required for the saponification of the fat, supplemented by Wanklyn's alcoholic-soda test. The numerical results are quoted under the name "acid-equivalent," which means the neutralising effect of 1 gram of fat expressed in equivalents of standard acid. 10 of the samples gave the odour of ethyl butyrate, with acid-equivalent

5.5 or above; these were "genuine;" with the other samples the odour is indistinct or absent; four of them are "doubtful" with acid-equivalent not below 5.0; the remainder with equivalent below this number are classified as "bogus."

D. A. L.

**Notes on Reichert's Method of Butter Analysis.** By L. W. McCAY (*Chem. News*, 50, 151).—With regard to this method of butter analysis, the author points out that the evaporation of the alcohol from the mixture of fat, caustic potash, and alcohol is essential, and is readily and effectually accomplished by applying suction to the interior of the flask whilst it is heated on the water-bath. As soon as the mass when shaken shows no tendency to froth, it may be dissolved in water, decomposed with acid, and distilled. The author prevents bumping during this operation by using small spirals of platinum wire with small pieces of pumice threaded and twisted on each end of the coil.

D. A. L.

**Methods of Butter Analysis.** By A. HANSEN and C. E. SCHMITT (*Bied. Centr.*, 1884, 707—710).—Hansen has made an exhaustive examination of the chief methods of butter analysis, and contributes the following notes on the subject. *Melting point.*—The addition of 15 per cent. of pure tallow raises the melting point from 33° to 36—37°, and the addition of 20 per cent. raises it to 38.5°, but the addition of tallow to the fatty acids obtained by Hehner's method causes no perceptible difference. *Heat* does not appear to affect the yield of insoluble fatty acids from either pure or mixed butter; after five hours' boiling, the author obtained 85.5 per cent. The loss of the acids in the process of saponification by alcoholic potash is extremely small, and is lessened by using absolute instead of dilute alcohol. In Hehner's method, the quantity of water employed in washing the precipitated fatty acids is important, if too little be used or insufficiently stirred, the volatile portions are not fully removed. The authors advise the use of 2 to 2½ litres, and always a constant quantity; from the wash-water of this process he obtained caprylic, capric, and caproic acids by evaporation with soda, distillation, separation of barium salts, &c., &c.

*Reichert or Meissl's Method.*—5 grams of the butter is saponified with potash and absolute alcohol in a flask with a reflux condenser; the alcohol is then distilled off, the last traces being removed by blowing air through; the acids are distilled with sulphuric acid, and the distillate titrated with decinormal soda; pure tallow required only 0.3 c.c., pure butter 29.6 c.c.; the number of c.c. found minus 0.4, multiplied by 3.42, gives the percentage of pure butter in the sample, viz. :—

			Butter fat.
15 per cent. added tallow	(25.0 c.c. — 0.4) × 3.42	=	84.5 per cent.
20       "       "	(23.3 c.c. — 0.4) ×       "	=	78.5       "
30       "       "	(20.3 c.c. — 0.4) ×       "	=	68.0       "

Koettstorfer's method, in which the alkalinity of alcoholic potash solution is diminished less by butter fat than other fats, is then men-



tioned. The author found the difference as follows—the figures being the amount of potash neutralised in milligrams:—

Butter fat.	20 per cent. tallow.	25 per cent. tallow.	30 per cent. tallow.
228·4	222·7	221·0	218·3

The authors think the Reichert method the best for the detection of tallow in butter, and next that of Koettstorffer.

Schmitt thinks that the Lechartier-Reichert system is the best; it consists in the distillation of volatile fatty acids from the saponified butter and titration of the distillate with phosphoric acid of 1·45 sp. gr. (10—12 c.c.); when the distillate amounts to 60 c.c. the condenser is washed with boiling alcohol and titrated with one-tenth normal soda; this operator multiplies the c.c. used by 0·352 to obtain the amount of butyric acid. J. F.

**New Reaction for Albuminoids.** By W. MICHAILOFF (*Chem. News*, 50, 242; from *Jour. Russ. Chem. Soc.*).—The reaction also serves for the nitrogenous and sulphuretted derivatives of the albuminoids. The substance in question is added to a solution of ferrous sulphate, treated with sulphuric acid (undiluted), and then cautiously mixed with a very small quantity of nitric acid. If nitrogen and sulphur are present there appear, along with the well-known brown rings, also rings of a blood-red colour, formed apparently at the expense of the nascent ferric oxide and of the thiocyanic acid formed simultaneously from the albuminoids by the action of the sulphuric acid. The appearance of a faint rose colour must be disregarded, as it is produced on merely mixing the reagents without any albuminoid body. J. T.

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## Technical Chemistry.

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**Clarification of Turbid River Water.** By LUEGER (*Dingl. polyt. J.*, **254**, 233—242).—The author discusses in detail the purification of water by filtration through sand. He states that the problem to be solved requires the settlement of the following questions:—(1) Is the existing sand adapted for the clarification of turbid water? (2) At what pressure (head of water) is the complete clarification effected? and (3) What is the magnitude of the total filtering surface for a certain quantity of water to be filtered? An important element in the success of the filtration of water through sand is the uniformity in the size of the grain of the sand. Sand differing in its degree of fineness admits of the filling up of the hollow spaces between the coarser grains by the finer particles, so that eventually the filtering surface is rendered impermeable by water.

D. B.

**Preparation of Sulphuric Anhydride from Nitrosyl Sulphate.**

By O. v. GRUBER (*Dingl. polyt. J.*, **254**, 139).—The author obtains sulphuric anhydride from the so-called chamber crystals, produced by interposing a series of small chambers between the Glover tower and the ordinary system of chambers. When the whole of the nitric acid is introduced into the system through the Glover tower at a density not under 58° B., the chambers contain the mixed gases in the proportion necessary to form the compound  $2\text{SO}_3, \text{N}_2\text{O}_3, 3\text{H}_2\text{O}$ . From Gay-Lussac towers this compound is obtained in a purer form. It may be prepared in small chambers specially constructed for this purpose, the chambers being fed with sulphurous anhydride and nitric anhydride. The resulting crystals are freed from all nitrogenous constituents by heating them in acid-resisting retorts and passing a current of dry air, or oxygen and sulphurous anhydride, through them. Thus liquid and, in some cases, solid sulphuric anhydride is produced, the percentage of anhydride depending on the dryness of the crystals attacked. The nitrogenous constituents are passed into a system of chambers, or recovered in the Gay-Lussac tower.

D. B.

**Composition of the Gases produced in the Combustion of Pyrites.** By SCHEURER-KESTNER (*Compt. rend.*, **99**, 917—919).—The amount of free oxygen present in the gases from pyrites burners is almost always somewhat less than that calculated from the composition of the original air and the amount of ferric oxide and sulphurous anhydride formed. In 1875, the author showed that this deficiency is due, *in part* at least, to the formation of sulphuric anhydride. In these earlier experiments the determinations of different constituents were made with different samples of the gases, and since the composition of the gases from the burners is somewhat variable, this method of procedure introduced sources of considerable error. He has therefore made further experiments, in which all the constituents were determined in the same sample of gas. A large volume of the gases from the burners was drawn through a standard solution of iodine until the latter was just decolorised. The amount of the sulphurous anhydride was thus obtained, and the amount of the sulphuric anhydride was estimated by determining the total sulphur in the iodine solution, and in a small wash-bottle containing water through which the gases passed on their way to the aspirator. The proportion of oxygen was ascertained by analysing the gas collected in the aspirator.

The results obtained show that the deficiency of oxygen in the burner gases is *entirely* accounted for by the proportion of sulphuric anhydride formed. In only two out of 15 experiments, and those of short duration, was sulphuric anhydride absent, whilst in the remaining 13 its proportion varied from 0.1 to 8.5 per cent.

C. H. B.

**Recovery of Hydrochloric Acid as a Bye-product in the Ammonia-soda Process.** By L. MOND (*Dingl. polyt. J.*, **254**, 220).—The liquors resulting from the separation of the bicarbonate are heated in a distillation apparatus to remove all volatile salts of ammonia. Instead of treating the fixed salts of ammonia with lime,

the liquors are concentrated by evaporation, and after the removal of the sodium chloride, the ammonium chloride is allowed to crystallise out. The latter is mixed with two equivalents of sulphuric acid, and heated in iron or leaden pans, the hydrochloric acid given off being condensed in the usual manner. The residue left in the pan, consisting of hydrogen ammonium sulphate, is converted into ammonium sulphate by treatment with gaseous ammonia obtained by distilling gas liquor. It may be used also for the manufacture of manures by mixing it with calcium phosphate in such proportions that the excess of acid in the salt is sufficient to dissolve all the insoluble phosphate present, and form superphosphate.

D. B.

**Consumption of Fuel in Blast Furnaces.** (*Dingl. polyt. J.*, 254, 167—177).—Fehland (Eisen and Stahl, 1884, 331 and 497) gives some data as to the time expended in the passage of the charges through the blast furnace, as this circumstance must be duly considered in calculating the capacity of blast furnaces.

In discussing the use of raw coal in blast furnaces, I. L. Bell states that some Pennsylvanian pits yield a variety of anthracite which, apart from what may be indicated by actual chemical composition, is only capable of performing a duty 10 per cent. below that of artificially prepared coke, and requires a more highly compressed blast, owing to the fact that it crumbles away on exposure to heat. For the purpose of illustration, a specimen of bituminous coal from the Brockwell seam in South Durham, gave by analysis—

C.	H.	O.	N.	S.	H <sub>2</sub> O.	Ash.
81.47	4.57	5.04	0.91	1.22	0.76	5.51

The coke made from the same coal contained 92.44 per cent. of carbon obtained by calculation. By the aid of Dulong's formula, a heating power of 7651 cal. was obtained for the coal, and 7395 cal. for the coke. To confirm the correctness of this calculation, Bell refers to the observations made by Donnell on the North Eastern Railway, who found that the consumption per mile of coal and coke by the same engine was practically the same. The volatile constituents of coal are, however, only partly oxidised in the blast furnace, but might be useful as a means of reducing the ferric oxide to the metallic state. As a further illustration, a description of the working of a blast furnace is given, using cannel coal from Lanarkshire, the furnace having a height of 22.5 metres, and being blown with air at 427°. The coal was analysed by Rocholl with the following results:—

	H <sub>2</sub> O given off at 100°.	C.	H.	O.	N.	S.	Ash.
	11.62	66.00	4.34	11.09	0.94	0.59	5.42
Volatile ...	—	12.59	4.34	11.09	0.94	—	—

The following figures contain the results of the analysis of the gases taken from the blast furnace:—

	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	C <sub>2</sub> H <sub>4</sub> .	H.
Per cent. by vol.....	6·29	29·04	2·84	0·24	6·83
„ by weight.	9·66	28·36	1·59	0·23	0·48
		N.	NH <sub>3</sub> .	H <sub>2</sub> O.	
Per cent. by vol.....		54·63	0·13	—	
„ by weight.		53·34	0·07	6·27	

The proportion of carbon as CO<sub>2</sub> to carbon as CO is as 1 is to 4·62, the escaping gases showed a temperature of 190°, whilst the blast averaged 427°. The charge consisted of the following mixture calculated on 100 parts pig iron :—

Coal.	Ironstone.	Limestone.
212·0	187·3	54·7

The carbon contained in the charge was as follows :—

Fixed carbon in the coal used.....	113·2
Carbon in the hydrocarbons .....	26·7
Carbon in the limestone .....	6·6
	<hr/>
	146·5
Deduct carbon absorbed by pig iron ..	3·5
Deduct carbon in tar.....	6·9
	<hr/>
Carbon in escaping gases.....	136·1

The weight of the escaping gases per 100 parts pig iron is as follows :—

		Carbon.	Oxygen.	Hydrogen.	Nitrogen.
CO <sub>2</sub> ....	81·3	22·1	59·2	—	—
CO ....	238·6	102·2	136·4	—	—
CH <sub>4</sub> ....	13·4	10·1	—	3·3	—
C <sub>2</sub> H <sub>4</sub> ...	1·9	1·7	—	0·2	—
H.....	4·0	—	—	4·0	—
O .....	448·9	—	—	—	—
NH <sub>3</sub> ....	0·6	—	—	0·1	448·9
H <sub>2</sub> O....	52·7	—	—	5·8	0·5
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	841·4	136·1	242·5	13·4	449·4

The quantity of heat developed is ascertained by the following calculation, whilst, for the purpose of comparison, the values of a furnace using 111·6 parts of coke are given, in which Cleveland calcined ironstone is smelted, the carbon in the coke employed being 102 parts :—

	Raw coal.	Coke.
Fixed carbon.....	113·2	102·0
Deduct carbon in limestone .....	6·5	8·2
Leaving carbon to develop heat....	106·7	93·8
Heat developed in burning carbon to carbonic oxide .....	256,080 cal.	225,120 cal.
Heat developed in burning part of the carbon to carbonic anhydride	124,040 „	182,560 „
Heat developed in burning the hydrogen .....	93,500 „	—
Heat contained in the blast.....	59,600 „	59,595 „
Total heat developed .....	533,220 „	467,275 „

*Appropriation of Heat.*

Fusion of slag .....	50,270 cal.	83,510 cal.
Decomposition of water .....	15,810 „	13,600 „
Expulsion and decomposition of the carbonic anhydride in the minerals	41,180 „	51,510 „
Evaporation of water.....	15,255 „	1,560 „
Expulsion of hydrocarbons.....	122,800 „	—
Reduction of the ferric oxide.....	163,550 „	165,540 „
Carbon contained in the pig iron. .	8,400 „	7,200 „
Reduction of silicon, phosphorus, and sulphur .....	21,330 „	20,870 „
Transmission through the walls of the furnace.....	27,435 „	18,290 „
Fusion of the iron.....	33,000 „	33,000 „
Carried off in cooling water.....	9,090 „	9,090 „
Carried off in escaping gases .....	44,765 „	55,215 „
	552,885 „	459,385 „

It will be perceived that in the case of the furnace using raw coal a much less oxidation of the carbon takes place, and in consequence a much smaller development of heat. The heating power of the carbon is, however, largely supplemented by the combustion of the hydrogen, but all the heat developed by the combustion of this gas, and far more, is absorbed in the act of expelling the volatile portions of the coal.

The reducing action of the blast furnace gases on sphaerosiderite ceases when one-third of the carbonic oxide has been converted into carbonic anhydride, so that, for example, on exposing Cleveland ore to the gases escaping from a furnace 20 m. in height little or no reduction was effected. In the case of the furnace using raw coal, these limits are far from being reached, for in its escaping gases the proportion was 4·62 parts of carbonic oxide to one of carbonic anhydride, or including the hydrogen and hydrocarbons, the ratio was 6·22 parts to one of carbonic anhydride. Of the carbon introduced into the furnace, it may be assumed that none of that contained in the hydrocarbons

reaches the neighbourhood of the tuyeres. Hydrogen, however, the result of the decomposition of atmospheric moisture, is always present in the gases at that place, whether the furnace is using coal or coke.

In using coke or coal, it is estimated that the carbon which ought to be found in the gases per 100 parts by weight of pig-iron is as follows:—

	Coke.	Coal.
Due to reduction of ferric oxide..	32·9 pts.	32·9 pts.
From decomposition of limestone.	8·2	6·5
Total .....	41·1	39·4
Actually found .....	32·6	22·1
Deficiency .....	8·5	17·3
Carbon in the coke .....	102·0	113·2
Deduct the carbon contained in the carbonic anhydride being resolved into carbonic oxide ....	8·5	17·3
Solid carbon in hearth .....	93·5 pts.	95·9 pts.

It will thus be seen that there is no great difference in the two examples as to the quantity of carbon which actually reaches the tuyeres for fusing the iron and slag. The advantage of working with lofty furnaces is the increased period of time during which the ore is exposed to the reducing action of the carbonic oxide at a temperature below that which suffices to have carbonic anhydride decomposed by carbon. This circumstance is said to be the cause of the disappearance of carbonic anhydride in the older furnaces used in Cleveland. Whilst a furnace 24 m. in height yields about 32·6 pts. carbon as carbonic anhydride per 100 pts. of iron, a furnace 15 m. in height yields only 27·4 pts. The disappearance of the carbonic anhydride in the Scotch furnaces is partly due to the presence of the hydrogen emitted by the coal. On passing hydrogen over limestone placed in a heated tube, Bell found that about one-half the carbonic anhydride was resolved into carbonic oxide, water being formed. The carbonic anhydride is reduced at the tuyeres, but the aqueous vapours generated are decomposed by the coal. The gases at the tuyeres of a Scotch furnace consisted of 1·43 per cent. carbonic anhydride, 32·96 carbonic oxide, 2·60 hydrogen, and 63·04 nitrogen. By adopting the nitrogen as the basis of the calculation, the carbon present works out to 103·2 instead of 106·7, as 448·9 parts of carbon are present for 100 pts. of pig-iron. In the case of the Scotch cannel coal, it may be assumed that the heat produced by the combustion of the gases contained therein will suffice for their own expulsion. 100 pts. coal should give 58·83 coke, consisting of 91·63 per cent. carbon, 0·50 water, and 7·87 ash. The quantity of heat required to smelt 100 kilos. pig-iron in the Scotch furnace, using the coal as coke, instead of raw coal, is estimated at 417,815 cal. The heat developed by burning one part of carbon to carbonic anhydride and 2·28 to carbonic oxide with a blast heated to 427°, amounts to 4587 cal. per kilo.

of carbon. This is equal to 91.1 kilos. carbon per 100 kilos. pig-iron, and by adding 3.5 per cent. carbon found in the pig-iron, 94.6 kilos. are obtained, corresponding with 103.25 kilos. coke containing 91.63 per cent. of carbon. But the coal actually used in the furnace contained 113.2 kilos. of fixed carbon, equal to 123.5 kilos. of coke, so that there is a waste of 18.6 kilos. carbon per 100 kilos. pig-iron when raw coal is used. The 18.6 kilos. of carbon, or, say 20 kilos. cannel coal, are not worth in the market above 15 pfennigs, which is less than the cost of converting this coal into coke.

In employing raw coal in blast furnaces, it must be borne in mind that for the condensation of the tar and ammonia given off by the coal, about thirteen times the quantity of gases has to be dealt with, as compared with the space occupied by the volatile constituents of the coal in the process of coking. It is said, however, that there is no more ammonia and tar obtained from a ton of coal distilled by Pease and Co., in the Carvé's oven, than is obtained by Baird and Co. from the coal used in the blast furnace, viz., about 9 kilos. ammonium sulphate, value 2.3s. and about 1.8s. worth tar; recently 13.6 kilos. sulphate and 102 kilos. tar have been obtained. D. B.

**Extraction of Nickel and Cobalt from its Ores.** By P. MANHÉS (*Dingl. polyt. J.*, **254**, 271).—It is proposed to separate the gangue accompanying sulphuretted and arsenical cobalt and nickel ores by fusion, and subject the product to a current of air in a Bessemer converter until almost the whole of the iron has disappeared. The residue contains from 15 to 20 per cent. of metalloids, and 1 to 2 per cent. of iron, the remainder being nickel, cobalt, and copper, which are separated in the usual manner (compare Abstr., 1884, 515).

D. B.

**Japanese Bronzes.** By G. MARQUARD (*Dingl. polyt. J.*, **254**, 138). The Bavarian Technological Museum at Nürnberg contains 18 plates of Japanese bronzes from Kioto, which have been recently examined by the author. He found that these plates were composed of five different alloys, which are recognised by a uniform mark on the face of each plate. The following analyses give the composition of the alloys arranged in accordance with the transition of colour from brass to pure copper:—

	Cu.	Sn.	Pb.	Zn.	Fe.	As.
1. Brass .....	73.28	—	0.79	25.71	traces	traces
2. O { mark of } ..	72.60	4.0	11.74	11.48	0.21	„
3. OO { the } ..	75.43	3.18	15.07	5.64	0.45	„
4. C { alloy } ..	82.17	3.96	13.34	0.28	0.24	„
5. Copper (containing traces of lead and iron).						

The high percentage of lead in the alloys was used probably to facilitate the mechanical treatment of the castings and the colouring by the aid of chemical agents. D. B.

**Nitrogenous Contents of American Beers.** (*Bied. Centr.*, 1884, 717).—Fifteen samples of beer were examined in the official laboratory at New York, the percentages of nitrogenous substance



in the extract ranged from a minimum of 7.5, to 14.5 with an average of 9.8, the variations are therefore within very wide limits.

J. F.

**Cultivated Wine Yeast.** By A. ROMMIER (*Compt. rend.*, 99, 879—880).—The author has extended his observations as to the effect of adding cultivated wine yeast to the must from different varieties of grapes, and has obtained results identical with those obtained with Chasselas (Abstr., 1884, 1399). The fermentation induced by adding the yeast takes place much more rapidly, and is complete in a far shorter time than the natural fermentation. The yeast should be added when it has attained full development.

C. H. B.

**Treatment of Syrups by Electricity.** By L. H. DESPEISSIS (*Dingl. polyt. J.*, 254, 209—211).—The author proposes to separate the alkalis and alkaline earths contained in saccharine juices by subjecting the latter to the action of an electric current. He claims to obtain an increase in the yield of sugar, and to recover the alkalis. The carbonates and saccharates of the juice are said to be decomposed by the influence of the electric current, carbonic anhydride and sugar being deposited at the positive pole, whilst the metals contained in the juice decompose the water which surrounds the negative pole, and are recovered in the form of bases.

The practicability of this process is doubted owing to the difficulty of effecting the separation of the alkaline earths, inasmuch as the resulting hydroxides which are deposited on the negative pole would interrupt the passage of the current in a very short time.

D. B.

**Animal Charcoal in Sugar-refining.** By H. PELLET (*Bied. Centr.*, 1884, 711—712).—Many refineries have ceased to use animal charcoal, employing instead the Puvrez filtration system, but it is found that the tubes soon become clogged, and the apparatus refuses to work; the author attributes this to the presence of silicic acid, and as this is not found in the beet it evidently is derived from the lime used in clarification, limestone itself containing certain proportions, and some being present in the ash of the coke used in burning the lime. Having analysed the residues of the *triple effet* evaporation system, he found in the first 0.40 per cent., in the second 23.40 per cent., and in the third 69.80 per cent. of silicic acid. Filtration of the juice through bone char removes the silica effectually, but soon renders the charcoal useless; the organic matter can be removed by reburning, but not the silica; the charcoal should be frequently changed and used as fresh as possible.

Gawalowski has found in 12 samples of limestone examined by him quantities of silicic acid varying from 0.10 per cent. up to 29.76 per cent.

J. F.

**Manufacture of Maltose by Dubrunfaut's Method.** By L. CUISINER (*Bied. Centr.*, 1884, 717—718).—Distilled water should be used, if possible. Should the water employed contain bicarbonate of lime or gypsum, it must be freed from them in order to avoid butyric fermentation; for the production of crystallised sugar, the purest

starch should be used; for syrups, flour, potatoes, and raw grain may be employed; the aqueous malt extract is best made from green malt. The starch is made into an emulsion with twice its weight of water, and after adding 5 per cent. of malt or its equivalent in extract, it is energetically stirred; in another vessel, water equal to 10 times the weight of the starch is heated to  $90^{\circ}$ , and both liquors poured simultaneously through a strainer, steam being blown through to complete mixing and solution; the temperature on entering the vessel is  $75^{\circ}$ , and when  $90^{\circ}$  is reached the mixture is as fluid as water and the operation is completed. The liquor is then cooled to  $40^{\circ}$ , malt extract added equal in malt to 10–15 per. cent. of the starch originally used, and the temperature maintained at  $40$ – $50^{\circ}$ ; after two or three hours, there is no reaction with iodine, and if syrup is wanted the process is interrupted at this point, but for solid maltose the temperature must be continued for 12 to 15 hours. If pure starch has been used, one filtration is sufficient, but in the case of rice and other materials the residue should be pressed; the liquor should now show a density of  $4^{\circ}$  Baumé; it is evaporated to  $20^{\circ}$  B., left to cool and clarify, and the clear yellow syrup is then filtered through ignited and washed charcoal from which it flows clear. It is finally evaporated to  $40^{\circ}$  B. in copper or tinned apparatus; at that density it is perfectly clear and mixes with water in all proportions without turbidity.

J. F.

**Report on Glucose.** By G. F. BARKER and others (*Chem. News*, 50, 196–198).—This is a report prepared for the Commissioner of Internal Revenue of the United States. The quantity of corn used for the manufacture of glucose in the States is estimated at 43,000 bushels per diem. The commercial products are of two kinds: (a) liquid, including glucose, mixing-glucose, mixing-syrup, corn-syrup, jelly-glucose, confectioners' crystal glucose; and (b) solid, including solid grape-sugar, chipped grape-sugar, granulated grape-sugar, powdered grape-sugar, confectioners' grape-sugar, and brewers' grape-sugar. Its uses are for the manufacture of table syrup; in brewing, instead of malt; in confectionery, instead of cane-sugar; as an adulterant of cane-sugar; for manufacturing artificial honey; and for making vinegar. The transformation of starch is generally effected by sulphuric acid; oxalic acid is, however, sometimes employed, and the use of phosphoric acid has been suggested. Liquid products contain more dextrin and maltose than the solid ones. The latter contain from 72 to  $73\cdot4$  per cent. of dextrose, and from  $4\cdot2$  to  $9\cdot1$  per cent. of dextrin, whilst the glucoses (liquid products) have  $34\cdot3$  to  $42\cdot8$  per cent. of dextrose, and  $29\cdot8$  to  $45\cdot3$  per cent. of dextrin. The contention amongst workers in Germany with regard to the prejudicial or non-prejudicial effect of the use of sugar (prepared from potato-starch) in brewing, &c., is entered into in some length, although no decidedly definite results were obtained. The authors then describe their own experiments, which consisted in submitting to very careful fermentation, with pure yeast, at a low temperature, ordinary barley worts, cane-sugar, and various samples of glucose. Five litres of the beer obtained in each of these fermentations was evaporated in most cases to 500 c.c., and at different times 200 c.c.

of each residue was taken internally by individuals, who did not suffer inconvenience in any of the cases investigated. From these results, it would seem that the products of the fermentation of glucose prepared from maize are not injurious to health; as, however, the experiments only lasted two months, it is still a question whether the continuous use of this substance might not cause injurious effects. It is also pointed out that although these products are not deleterious, it does not follow that beer brewed from glucose is as good as that made in the usual way.

D. A. L.

**Some Constituents of Emmenthaler Cheese.** By B. RÖSE and E. SCHULZE (*Landw. Versuchs-Stat.*, **31**, 115—137).—This work is a supplement to Weidemann's paper on the changes undergone by Emmenthaler cheese during the process of decay, and is chiefly confined to a qualitative examination of the products formed. Ether extracts a fat which proved to be a glyceride, but was not further analysed, also lactic acid and a small quantity of cholesterin. The residue, after treatment with ether, consists mainly of albuminoids and their decomposition products, together with sundry salts. Leucine is obtained in quantity by treating the residue with 70 per cent. alcohol, and may be purified by repeated crystallisation from alcoholic ammonia; tyrosine and lactic acid are also to be found in this residue, although in small quantities, and the presence of other organic acids was also noted. Caseoglutin is found in the alcoholic extract in considerable quantity, and can be precipitated by the addition of absolute ether and alcohol, as it is insoluble in a 90 per cent. solution of the latter. Its analysis gave the following results:—Carbon, 54.4; hydrogen, 7.34; nitrogen, 15.29; sulphur, 0.95; and oxygen, 22.02 per cent. Its alcoholic solution dries in the air to a transparent mass having the appearance of glue. Phosphotungstic acid and tannin throw down caseoglutin completely from its solutions; the latter are optically active, and laevorotatory. The products of decomposition of caseoglutin are glutamic acid, tyrosine, leucine, and asparagine.

The albumen left after treatment of the cheese successively with ether and alcohol was found to differ very slightly from the purified albumin precipitated from milk by rennet, and called by the authors paracasein. Both, when treated with pepsin, throw down a precipitate of nuclein, and they yield nearly the same figures on analysis, the slight difference being probably due to their not containing quite the same amount of nuclein.

J. K. C.

**Action of Bisulphites on Chlorates.** By PRUDHOMME (*Dingl. polyt. J.*, **254**, 226).—On treating sulphurous anhydride with chloric acid, sulphuric and hydrochloric acids are formed. The bisulphites of the alkalis, however, reduce the chlorates only in a very imperfect manner, as shown by the following equation:— $\text{NaClO}_3 + \text{NaHSO}_3 = \text{HClO}_2 + \text{Na}_2\text{SO}_4$  and  $\text{NaClO}_3 + 2\text{NaHSO}_3 = \text{HClO} + \text{Na}_2\text{SO}_4 + \text{NaHSO}_4$ . The resulting hydrogen sodium sulphate may be made to react with further portions of bisulphite, sulphurous acid being disengaged. On adding a solution of sodium bisulphite to a concentrated

solution of sodium chlorate (100 grams per litre), a violent action occurs, especially if the solution of chlorate is hot. A strong odour of chlorine oxides and of sulphurous acid is given off, and the solution will be found to destroy the colour of indigo and other dye-stuffs, and convert cellulose into hydroxycellulose. With salts of aniline, the solution forms aniline-black, a reaction which confirms Rosenstiehl's theory as to the formation of aniline-black. When chlorates and bisulphites act on one another in the presence of alcohol, chlorinated ethers are formed.

D. B.

**New Chrome-mordanting Process.** By H. KOEHLIN (*Dingl. polyt. J.*, **254**, 132).—This process depends on the fact that when solutions of chromium salts saturated with alkalis are brought into contact with the fibre, the chromium oxide is at once given up to the latter without the necessity of drying.

The fabric is digested for 12 hours in a bath containing 2 parts (by vol.) of chromium acetate (16° B.), 2 parts soda-lye (36°), and 1 of water. It is then washed thoroughly with water. Ferric oxide may be fixed on the vegetable fibre in a similar manner, but owing to the insolubility of  $\text{Fe}_2(\text{OH})_6$  in alkalis, the precipitation of the hydroxide should be prevented by adding certain organic substances. The following mixture gives good results:—2 parts ferric nitrate (40°), 2 soda-lye (36°), and 1 glycerol (28°).

D. B.

**Formation of Hydroxy- and Chloro-cellulose Electrochemically.** By F. GOPPELSROEDER (*Dingl. polyt. J.*, **254**, 42—43).—The author gives the first results of an investigation of changes produced electrochemically in cotton and linen fibre. A cotton or linen fabric, soaked in a neutral, acid, or alkaline solution of potassium nitrate or sodium chloride, is laid on a similarly soaked cloth, resting on a negative platinum electrode; on placing the positive electrode in contact with the fabric for a shorter or longer time, the products set free at the positive electrode by the current, produce such a change in the fibre that certain dyes are much more readily fixed than in the unchanged portions.

J. T.

**Preparation of the Sulphonic Acids of Methyl Violet.** (*Dingl. polyt. J.*, **254**, 140.)—To prepare the sulphonic acids of methyl violet (*violet de Paris*), an excess of sulphuric acid has to be used, which is subsequently neutralised with calcium hydroxide, the resulting solution being evaporated. During the process of evaporation, the dye is partly decomposed. According to the *Société Anonyme des Matières Colorantes et Produits Chimique de St. Denis in Paris* (Ger. Pat. 28,884, December, 1883), the excess of acid is completely or partly converted into soluble sulphates such as potassium, sodium, ammonium, magnesium, or zinc sulphate. The colouring matter is then treated with a small quantity of water sufficient to form a paste therewith.

D. B.

## General and Physical Chemistry.

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**Coloration of the Hydrogen Flame.** By S. SANTINI (*Gazzetta*, 14, 142—146).—It is generally stated that hydrogen burns with a colourless flame; but it is here shown that under certain conditions the flame is coloured, and that this effect does not result from impurities in the materials used for generating the gas. The phenomenon is the more marked if a tube is placed over the flame, as in the chemical harmonicon, when the various colours of the spectrum can be observed by varying the conditions of the experiment. In general the centre of the flame is green, while the external envelope is of a violet-blue colour; by reducing the pressure of gas, the blue colour becomes green, and then successively yellow, orange, and red. Thus, by decreasing the intensity of the combustion, whether by the less direct contact of the oxygen with the hydrogen in the centre of the flame, or by a diminution of the pressure, the refrangibility of the emitted light decreases. The author considers that the variations of the solar spectrum may arise from differences in the density, and consequently of the luminosity of the hydrogen contained within the solar photosphere. V. H. V.

**Influence of Temperature on Spectroscopic Observations and Measurements.** By G. KRÜSS (*Ber.*, 17, 2732—2739).—In the experiments described in this paper, the room in which the observations were made was heated to various temperatures, at which it was kept constant for some hours, the observations being taken when it was ascertained that the temperature of the spectroscope was the same as that of the surrounding air. Comparative experiments are described with a 60° glass prism, a 60° quartz prism, and a Rutherford grating, and these show that very appreciable errors may be introduced by a difference in temperature of 25°:—

	C.	$\frac{D_1 + D_2}{2}$	E.	<i>b</i> .	F.
60° glass prism . . . . .	+ 7·50	+ 7·67	+ 9·83	+ 7·50	+ 9·33
60 quartz prism . . . . .	—	— 4·10	— 2·27	— 6·36	— 4·32
Rutherford grating . . .	+ 8·28	+ 9·06	+ 9·53	+ 9·06	+ 13·75

The figures represent the amount of deviation in units of the scales employed, the sign + indicating that the deviation is towards the violet, the sign — that it is in the opposite direction; the mean error of observation is about 0·31 unit, whilst the deviation for 1° is 0·366 unit. The following table shows a comparison in wave-lengths, T being the scale-number:—

T.	$\lambda$ (at 5°).	$\lambda_1$ (at 30°).
1169·4	656·8	658·9
1432·9	589·7	592·0
1801·5	527·4	529·0
1863·1	517·7	519·2
2144·8	486·5	488·0

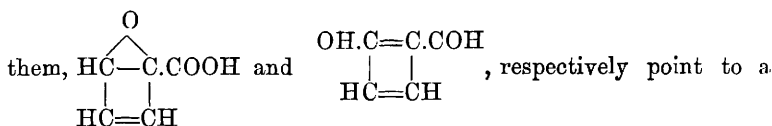
A. K. M.

**Specific Refraction in Reference to the Double Bond.** By R. NASINI (*Gazzetta*, 14, 150—156).—The author, in association with Bernheimer, has shown, principally from experiments on the naphthalene-derivatives and cinnamic acid, that Brühl's hypothesis that each pair of carbon-atoms, combined together as in the olefines (the so-called double bond) increases the molecular refraction (*Gazzetta*, 13, 137) is incorrect. Recent experiments by Kanonnikoff on the same class of derivatives tend, however, to confirm this hypothesis. The cause of this discrepancy is examined in the present memoir. The difference in the results arises from the fact that Kanonnikoff used solutions of those substances, whereas Nasini's and Bernheimer's experiments were conducted with the solids or liquids themselves, a process more likely to give trustworthy results.

On a comparison of the results obtained with cinnamic acid, naphthalene, bromonaphthalene, and  $\alpha$ -naphthol, the difference of the value for A is in one case more than 2 units, or practically equal to the supposed difference produced for each pair of double-linked carbon-atoms. Kanonnikoff's experiments, however, show that the difference of 2 units is not constant, but in certain naphthalene-derivatives a difference of 3·6 units is noticed, a result which is explained away by the great dispersive power of these substances (see Gladstone, *Trans.*, 1884, 254—259). In the case of naphthalene tetrachloride, whose dispersive power is certainly not greater than that of many benzene-derivatives, the increase of specific refraction A is 8·66 instead of 6 units as required by Brühl's hypothesis. The only argument which might tend to explain these abnormal variations is the want of exactness in the constant A, but even this would militate against rather than support Kanonnikoff's views; for the values for A and of  $P \frac{A-1}{d}$  increase with the number of constants used for their calculation, as for example:—

	A (two constants).	A (three constants).	$P \frac{A-1}{d}$ (two constants).	$P \frac{A-1}{d}$ (three constants).
Dimethylnaphthalene	1·5637	1·57476	87·02	88·73
Methyl- $\alpha$ -naphthol ..	1·5721	1·58953	82·44	84·29

In conclusion, Kanonnikoff's views regarding the constitution of furfuraldehyde and pyromucic acid, based on the determinations of their molecular refraction, are criticised, for the formulæ assigned to



wide difference of constitution, although, in its reactions, furfuraldehyde comports itself as the aldehyde corresponding with pyromucic acid.

V. H. V.

**Refractive Power of the Hydrocarbon  $\text{C}_{12}\text{H}_{20}$ .** By A. ALBITZKY (*J. pr. Chem.* [2], 30, 213—214).—This hydrocarbon was prepared from allyl dimethyl carbinol by Nikolsky and Saytzeff's method (Abstr., 1879, 214). The sp. gr. and refractive indices were determined with a portion boiling at 195—199°. The specific refraction shows that in this hydrocarbon three of the carbon atoms are united by double linkage.

The following are the results of the determinations:—Sp. gr. at 0° = 0.8512, at 9.8° = 0.8449, at 21.4° = 0.8349, at 18.4° (calc.) = 0.8381 (water at 0° = 1).

Refractive indices for hydrogen lines  $\alpha$ ,  $\beta$ ,  $\gamma$ , and for sodium line D at 18.4° are:—

$n_{\alpha}$ .	$n_{\text{D}}$ .	$n_{\beta}$ .	$n_{\gamma}$ .	A.	B.
1.47286	1.47683	1.48537	1.49369	1.45667	0.69829

$\frac{A - 1}{d}$ .	P $\frac{A - 1}{d}$ .	$R_{\text{A}}$ .	Difference.
0.5448	89.34	84.12	5.22

P. P. B.

**Dispersion of Sodium Chromate.** By G. WYROUBOFF (*Jahrb. f. Min.*, 1885, 1, Ref., 25).—This salt, sodium chromate with  $4\text{H}_2\text{O}$ , described by the author in 1880, is remarkable for its strongly inclined dispersion of the bisectrices and strong dispersion of the axes. The acute positive bisectrix forms with  $\hat{a}$ , in the obtuse angle  $\beta$ , an angle of 10° 21' for red light, and 7° 49' for green light. The angle of the axes is 16° 10' for red, and 32° 22' for green (in air). Well prepared specimens in Canada balsam last for a considerable time.

B. H. B.

**Electric Conductivity of Amalgams.** By C. L. WEBER (*Ann. Phys. Chem.* [2], 23, 447—476).—The experiments of Matthiessen and Vogt on the influence of a foreign metal on the conductivity of mercury, led to no satisfactory results, owing to the difficulty experienced in the production of a homogeneous material. The experiment herein detailed, shows that the conductivity of amalgams of tin and mercury increases with increase of temperature, and *vice versa*;

but that these changes are regular when a small percentage of tin only is added.

The thermoelectric positions of various amalgams of copper are also compared with that of pure mercury; the presence of the foreign metal in all cases diminishes the difference of potential. Those examined may be arranged in the following series (if 0.5 gram of the metal be added to 100 grams of mercury): tin, silver, lead, zinc, cadmium, and bismuth. The specific resistance of the combination decreases with increase in the amount of metal added. A comparison of the galvanic resistance and thermoelectric difference of potential shows that in all cases, with the exception of cadmium, increase of the former is correlated with increase of the latter.

In conclusion, the author remarks on the advantage of mercury as the metal for comparison in thermoelectric series, as reproducible in a homogeneous state, and as the only metal which shows no difference of potential when one portion is warmed and the other cooled.

V. H. V.

### Electric Conductivity of Solution of Carbonic Anhydride.

By E. PFEIFFER (*Ann. Phys. Chem.* [2], **23**, 625—650).—The experiments of Hittorf on the migration of the ions during electrolysis point to the importance of electric functions in deciding the chemical constitution of solutions of gases in water. Kohlrausch has also proved by experiments on the electric conductivity of solutions of ammonia, that these do not contain the hypothetical combination—ammonium hydrate. In this paper, an account is given of experiments on solutions of carbonic anhydride under increased pressures varying from 1 to 25 atmospheres. The following are the principal results:—

(i.) A solution of carbonic anhydride in water forms one of the worst conductors known: the conductivity under normal conditions being about one-twentieth of that of spring-water.

(ii.) Although it is commonly assumed that a solution of carbonic anhydride in water contains the hypothetical carbonic acid,  $\text{H}_2\text{CO}_3$ , in that it possesses an acid reaction, yet according to Kohlrausch's experiments the conductivity of such a combination should be equal to  $202,000 = 10^{-10}$  C.G.S. units, or more than a thousand times greater than the highest value found.

(iii.) Change of pressure produces no alteration in the conductivity, which would appear to show that the carbonic anhydride is liquefied in the process of solution.

(iv.) Carbonic anhydride is soluble in water at temperatures above its critical point; if then the solution were a mixture of water and liquid carbonic anhydride, it is probable that irregularities in its conductivity would be observed at the critical point, but this is not the case.

(v.) The curve of the conductivity as a function of the temperature is analogous to the curves described by Kohlrausch for oxalic, tartaric, and acetic acids, in that it ascends rapidly for increase of dilution. This would seem to point to an analogy of constitution of a solution of carbonic anhydride in water with these acids.

V. H. V.



**Influence of Magnetisation on the Resistance of Magnetic Liquids.** By F. NEESEN (*Ann. Phys. Chem.* [2], 23, 482—493).—Former experiments on the influence of magnetisation on the conductivity of magnetic liquids have led to negative results. In this paper, an account is given of an investigation on the effect produced by the magnetisation of ferrous sulphate as regards its electric conductivity. It would appear, so far as the experiments would permit of a conclusion, that if the lines of the magnetic field are normal to the direction of the electric current, no effect is produced, but if the two are parallel to one another, the electric conductivity is increased and eventually the electromotive force of the polarisation of the liquid appears to be diminished. V. H. V.

**Diathermancy of Æsculin.** By K. WESENDONCK (*Ann. Phys. Chem.* [2], 23, 548—553).—Lommel has concluded from his researches that fluorescent substances are divisible into two classes; the members of the one display marked absorption-bands in the visible part of the spectrum, but do not follow Stokes' law, while those of the other, although in accordance with that law, do not show these absorption phenomena in such a marked degree. The author has examined whether in substances of the second class, of which æsculin was selected, absorption-bands cannot be detected in the ultra-red portion of the spectrum, but the results obtained were negative. V. H. V.

**Tension of Aqueous Vapour of Hydrated Salts.** By W. MÜLLER-ERZBACH (*Ann. Phys. Chem.* [2], 23, 607—625).—The experiments of Naumann and Kraus on the tension of water-vapour evolved in a Torricellian vacuum from hydrated salts, led to unsatisfactory results, owing to the reabsorption of the emitted water by the partially dehydrated salt, when the tension of the former had reached a certain point. The observations are also complicated by the concomitant alterations of the tension of the vapour of mercury. The method described in this paper is based on a comparison of the loss experienced, by two suitably constructed tubes of the same dimensions, the one containing the salt to be examined, the other distilled water, both enclosed over sulphuric acid. In the experiments herein described it is shown that there is practically a constant ratio between the diminutions in weight experienced by the tube for each definite combination of the salts with their water of crystallisation. Thus a convenient method is presented for determining the nature and degree of combination of the molecules of water with the molecules of salt. The following results were obtained:—There are three definite compounds of disodium hydrogen phosphate, with 2, 7, and 12 mols.  $\text{H}_2\text{O}$  respectively; two compounds of sodium carbonate with 1 and 10 mols.  $\text{H}_2\text{O}$ ; two compounds of sodium borate with 5 and 10 mols.  $\text{H}_2\text{O}$ . The 10 mols.  $\text{H}_2\text{O}$  of crystalline sodium sulphate seem to be combined in an equal degree. The last molecules of water of crystallisation of sodium phosphate and carbonate are removed by a sufficiently long exposure over sulphuric acid (comp. Abstr., 1884, 952). V. H. V.

**Condensation of Carbonic Anhydride on Glass.** By H. KAYSER (*Ann. Phys. Chem.* [2], **23**, 416—426).—Bunsen's researches on the condensation of carbonic anhydride on glass are in direct opposition to former observations (comp. Abstr., 1884, 146), in that he found that the phenomenon was incomplete after three years, that alteration of pressure was without effect, and that the condensation increased with rise of temperature. The author has repeated these experiments with the following results:—(i.) The condensation is completed a short time after the introduction of the gas, provided that the glass surface is perfectly free from other gases; other less condensible gases are ousted by the carbonic anhydride. (ii.) The quantity of gas condensed increases with rise of pressure and decreases with diminution of pressure; it increases with diminution of, but decreases with rise of temperature. These results are in accordance with former observations with other gases. The author remarks on the inadvisability of applying the name "diffusion" to this phenomenon of the condensation, or "absorption" of gas on glass: for the former term is applied to the most various phenomena. The name "penetration" is proposed as more applicable and suggestive.

V. H. V.

**Combustion of Hydrocarbons and their Oxides and Chlorides with Mixtures of Chlorine and Oxygen.** By G. SCHLEGEL (*Annalen*, **226**, 133—174).—It has been shown by Bötsch (Abstr., 1882, 456), that in the explosion of a mixture of hydrogen, oxygen, and chlorine, water is formed only when the chlorine is present in amount insufficient to unite with the whole of the hydrogen; this result is important, inasmuch as it does not agree with the generally accepted rule that when several substances react simultaneously on one another those reactions always occur in which the greatest amount of heat is developed. The author has extended these researches to the products of the explosion of mixtures of chlorine and oxygen with gaseous organic compounds. Experiments were made with excess both of chlorine and oxygen, with an excess of oxygen and an amount of chlorine insufficient to unite with all the hydrogen present, and finally with an excess of chlorine, but with an amount of oxygen insufficient to convert the whole of the carbon into carbonic anhydride. The organic substances employed were methane, ethane, propane, butane, methyl ether, methyl chloride, ethyl chloride, acetylene, and carbonic oxide. No results could be obtained with ethylene, as it unites with chlorine in the dark, and so prevents the formation of an uniform mixture for explosion. The following are the conclusions drawn from these experiments:—(1.) If a hydrocarbon be mixed with excess of chlorine and excess of oxygen and the mixture exploded by the spark, the whole of the carbon is converted into carbonic anhydride and all the hydrogen into hydrochloric acid. Hydrogen does not unite with oxygen nor carbon with chlorine. (2.) If excess of oxygen be employed together with an amount of chlorine insufficient to combine with all the hydrogen present, then the remainder of the hydrogen unites with oxygen. (3.) If with excess of chlorine the amount of oxygen is insufficient to convert all the carbon into carbonic anhydride, there is then also formed carbonic

oxide, the proportion of this latter increasing with the deficiency of oxygen. (4.) If neither chlorine nor oxygen is present in sufficient quantity for complete combustion, carbon is separated. (5.) The organic chlorides and oxides experimented with behaved in like manner to the hydrocarbons.

A. J. G.

**Determination of Specific Gravity of Carbonic Acid Solution.** By A. BLÜMCKE (*Ann. Phys. Chem.* [2], **23**, 404—415).—Observations on the change of volume in a liquid produced by the absorption of gases have for the most part been made under normal atmospheric conditions. In this paper a method is described, on the hydrostatic principle, by means of which the sp. gr. of solutions of carbonic acid under increased pressure can be determined. A series of these determinations are given, made under pressures varying from 2 to 37 atmospheres; in all cases it appeared that the absorption of the gas was the more marked the greater the initial pressure. The results point to the following empirical formula for the sp. gr. of solutions of carbonic acid:  $S = \frac{1 + n \cdot 001965}{1 + n \cdot 001568}$ , in which

0·001965 is the weight in grams of 1 c.c. of carbonic anhydride, and 0·001568 is the constant deduced from the experiments. Hence the addition in volume by the absorption of carbonic anhydride is directly proportional to the gas absorbed, if the compressibility of the liquid by increase of pressure is neglected. Although the results show a remarkable diminution in volume experienced by the carbonic anhydride in its absorption by water, yet no conclusive proof is offered of the liquefaction of the gas in the course of solution, especially as Andrews' experiments show that the critical point of a gas is lowered by its admixture with another gas or vapour of a volatile liquid.

V. H. V.

**Crystallisation.** By C. MARIGNAC (*Ber.*, **17**, 2831—2832), and by O. LEHMANN (*Ber.*, **17**, 2885—2886).—Replies to Brügelmann (this vol., p. 114).

**Lecture Experiments.** By A. VALENTINI (*Gazzetta*, **14**, 214—218).—In this paper various forms of apparatus are described for the combustion of substances in oxygen, and chlorine; the preparation of ozone by Schönbein's method; the preparation of chlorine; the combustion of ammonia in oxygen, and chlorine; and the oxidation of ammonia. Drawings of the various pieces of apparatus are given.

V. H. V.

### Inorganic Chemistry.

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**Action of the Induction Spark on Phosphorus Trifluoride.**  
By H. MOISSAN (*Compt. rend.*, **99**, 970—972).—When carefully dried phosphorus trifluoride is subjected to the action of induction sparks, the volume of the gas *diminishes*, and phosphorus is deposited on the

sides of the eudiometer. The glass is not attacked, and the gas contains no trace of silicon fluoride. When brought in contact with water, about 6—7 per cent. of the gas is dissolved, yielding a solution which contains phosphoric acid, whilst the residual gas has all the properties of phosphorus trifluoride. It would seem, therefore, that the induction spark partially decomposes phosphorus trifluoride into phosphorus and fluorine, but that the latter at once unites with undecomposed trifluoride, forming phosphorus pentafluoride. If the passage of the spark is continued for several hours, the deposit of phosphorus increases, and the volume of the residual gas continues to diminish; after some time, however, a condition of equilibrium is attained and decomposition ceases.

If the phosphorus trifluoride is not completely dried, but is simply bubbled through strong sulphuric acid and then subjected to the action of the spark, phosphorus is liberated and the volume of the gas diminishes, whilst the eudiometer is corroded, and after an hour the residual gas contains as much as 20 per cent. of silicon fluoride. The small quantity of water in the gas is decomposed by the spark, and the hydrogen unites with some of the fluorine of the trifluoride, forming hydrofluoric acid, which acts on the glass and thus produces silicon fluoride and water. This water is decomposed in the same manner, and the same series of reactions again takes place, a small quantity of water being thus sufficient to convert a relatively large quantity of phosphorus trifluoride into silicon fluoride. This conversion is, however, never complete, a condition of equilibrium being established after some time. The mixture of gases resulting from the action of the spark on moist phosphorus trifluoride gives a deep blue coloration when brought in contact with potassium iodide and starch. No similar coloration is given by the products of the action of the spark on the dry gas.

C. H. B.

**Density of Sulphuric Acid.** By G. LUNGE (*Ber.*, **17**, 2711—2715).—A reply to Mendeléeff.

**Pyrosulphates.** By H. SCHULZE (*Ber.*, **17**, 2705—2709).—By heating normal sulphates with sulphuric anhydride in sealed tubes, Weber obtained octosulphates (this vol., p. 121); these are converted by heat into pyrosulphates. The author finds that many sulphates combine with sulphuric anhydride without the application of heat, and that when the excess of anhydride is distilled off at 100—120°, pyrosulphates remain more or less pure. Potassium, ammonium, silver, and thallium pyrosulphates may thus be obtained pure, and also those of the alkaline earths and of magnesium, but the product from sodium sulphate contains only 85 per cent. pyrosulphate. The sulphates of lead, zinc, cobalt, nickel, and manganese also absorb sulphuric anhydride to a greater or less extent.

Attempts to prepare barium and magnesium pyrosulphates by heating their hydrogen sulphates yielded negative results. Hydrogen ammonium sulphate heated at 250—300° gave a product containing 74·44 per cent.  $\text{SO}_3$  (calculated for pyrosulphate, 75·47). Better

results are obtained by heating sulphates with chlorosulphonic acid (see Schiff, *Annalen*, **126**, 168); the author has prepared sodium, ammonium, and barium pyrosulphates in this way. A. K. M.

**Comparative Oxidation of Solutions of Sulphurous Acid and of Sodium Sulphite.** By C. L. REESE (*Chem. News*, **50**, 219).—In these experiments, solutions of sodium sulphite and of sulphurous acid of various strengths were exposed to daylight and air in green glass bottles, the neck of each being closed by a cork through which a short open tube 2 mm. wide passed, and was bent outside to exclude dust. The solutions of sodium sulphite were of strength equivalent to 21.10, 3.77, and 0.765 parts of sulphurous anhydride to 1000 of water respectively, whilst the solutions of sulphurous acid contained 6.00 and 1.063 parts of sulphurous anhydride in 1000 parts of water. During the experiments, the temperature varied frequently between 50° and 90°. It was found that the weaker solutions oxidise more rapidly than the more concentrated; that with weak solutions the sulphite is oxidised more rapidly than the sulphurous acid; that with stronger solutions the smaller rate of oxidation of the sulphurous acid was more than compensated by loss due to the diffusion of sulphurous anhydride into the air. D. A. L.

**Atomic Weight of Cerium.** By H. ROBINSON (*Proc. Roy. Soc.*, **37**, 150—156, and *Chem. News*, **50**, 251—253).—The author has made seven very careful determinations of the chlorine in a very pure preparation of cerium chloride; the mean of the results obtained gives 139.9035 as the atomic weight of cerium, the atomic weight of hydrogen being taken as unity and Stas's ratios employed; if oxygen is taken at 16, the above number becomes 140.2593. Much care and labour was bestowed on the preparation of the cerium chloride, which was made from pure cerium oxalate by passing pure hydrochloric acid over it, first at a temperature of about 123°, subsequently at a red heat. The purification of the oxalate was only effected by many laborious operations. A full description of these operations and of the method of determining the chlorine is given in the paper.

D. A. L.

**Action of Lead Hydroxide and Silver Oxide on Aqueous Solutions of Sodium Pentasulphide and Sodium Thiosulphate.** By A. GEUTHER (*Annalen*, **226**, 232—240).—When an aqueous solution of sodium pentasulphide is vigorously agitated with lead hydroxide at the ordinary temperature, lead sulphide and sodium hydroxide are formed and sulphur liberated, according to the equation:  $3\text{Na}_2\text{S}_5 + \text{Pb}_3\text{O}_4\text{H}_2 + 2\text{H}_2\text{O} = 6\text{NaOH} + 12\text{S} + 3\text{PbS}$ ; a trace of thiosulphate is also formed. Silver oxide, under like conditions, behaves similarly to lead hydroxide, but some quantity of sulphate is also formed, owing to the powerful oxidising action exerted by the silver oxide on sulphur. Sodium dithionite in aqueous solution, when agitated in the cold with silver oxide, is first decomposed according to the equation  $2\text{S}_2\text{O}_3\text{Na}_2 + \text{Ag}_2\text{O} + \text{H}_2\text{O} = \text{S}_2\text{O}_3\text{Na}_2 + \text{S}_2\text{O}_3\text{Ag}_2 + 2\text{NaOH}$ , only a trace of sulphuric acid being formed; after a time, the alkalinity of the liquid diminishes, owing to a further reaction, in which

silver sulphide and sodium sulphate are formed. The author points out that these results confirm the opinion expressed by Böttger (Abstr., 1884, 342), that the pentasulphides and thiosulphates cannot be correctly regarded as sulphates in which oxygen has been replaced by sulphur. A. J. G.

**Action of Hydrogen Phosphide on Bismuth Trichloride.**

By A. CAVAZZI (*Gazzetta*, **14**, 219—220).—If a current of hydrogen phosphide is passed into a solution of bismuth trichloride in hydrochloric acid, and water added from time to time, a black precipitate is produced containing chlorine, phosphorus, and bismuth. In an experiment cited, the quantity of hydrogen phosphide absorbed, corresponded with the production of a bismuth phosphide containing one atom of each element. The author considers it probable that a hydrochloride of this compound is first formed, but that this on desiccation loses hydrogen without at the same time losing chlorine. On frequent boiling with water, it yields metallic bismuth, and is converted into the sulphate and nitrate of the metal by treatment with sulphuric and nitric acids. When heated, it ignites at a comparatively low temperature, leaving a residue of bismuth. V. H. V.

**Action of Tellurous and Telluric Acids on Paratungstates.**

By D. KLEIN (*Bull. Soc. Chim.*, **42**, 169—170).—Tellurous acid,  $H_2TeO_3$ , dissolves readily in solutions of sodium, ammonium, or potassium paratungstate, yielding in the first case micaceous crystals and a dense mother-liquor. This mother-liquor gives no precipitate with hydrochloric acid in the cold, and is only decomposed after several successive evaporations to dryness with this acid. The mother-liquor contains tellurous acid, which is only precipitated by sulphurous acid or hydrogen sodium sulphite in the cold, after addition of hydrochloric acid.

The action of tellurous acid on ammonium or potassium paratungstate yields no crystalline products, but only a pulverulent deposit, which contains tungstic and tellurous acids, and behaves like a tungstotellurite.

When telluric acid,  $H_2TeO_4$ , acts on potassium paratungstate, a crystalline compound is formed which contains tungstic and telluric acids and potassium.

It is evident that the behaviour of the acids of tellurium towards the alkaline tungstates is very different from that of the acids of sulphur. C. H. B.

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### Mineralogical Chemistry.

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**Determination of the Coefficient of Cubic Dilatation of Minerals.** By J. THOULET (*Jahrb. f. Min.*, 1885, **1**, Ref., 16—17).—Thoulet has already employed with advantage the high sp. gr. (3·2) of a concentrated aqueous solution of potassium mercury iodide.



From this, solutions may easily be prepared with sp. gr. 3.2 to 1.0. In the meantime, V. Goldschmidt has estimated the cubic dilatation of mercury iodide solution at various degrees of concentration, and the table he has drawn up is employed by Thoulet for a method of determining the coefficient of cubic dilatation of isotropic minerals in small fragments.

A funnel-shaped vessel is closed below by a cork, and in this is placed a thin test-tube, about 110 mm. high and 35 mm. in diameter. The vessel is placed on a sand-bath and heated by a gas burner. The test-tube serves for the reception of the small fragments of mineral and a solution of mercury iodide of rather lower density than that of the mineral at the maximum temperature employed. The surrounding space, enclosed by the walls of the funnel, serves as a water-bath. The vessel is slowly cooled, and the temperature  $t^1$  observed, at which the mineral fragment, placed at the bottom, begins to float. The density of the mineral  $D^1$  at the temperature  $t^1$  may then be determined from the density of the solution  $D$  at the temperature of the laboratory  $t$  and from Goldschmidt's table. In a similar way, the density  $d$  is taken at the minimum temperature  $t$ . The solutions of mercury iodide employed at the temperature  $t$  and  $t^1$  will vary but very slightly, so that to both solutions the same coefficient of dilatation  $\alpha$  may be assigned. Then—

$$\frac{D^1}{D} = \frac{1}{1 + \alpha(t^1 - t)}$$

$$\frac{D^1}{d} = \frac{D}{d(1 + \alpha(t^1 - t))}.$$

The coefficient of dilatation of the mineral is then

$$k = \frac{1 + \alpha(t^1 - t)d - D}{(t^1 - t)D}$$

As a rule, the coefficient of dilatation is given for  $0^\circ$ , so that the formula for  $\frac{D^1}{D}$  would be

$$\frac{D^1}{D} = \frac{1 + \alpha t}{1 + \alpha t^1}.$$

For all practical purposes, the approximate formula given above will be enough. B. H. B.

**Silver Amalgam from Oberlahnstein.** By v. DECHEN (*Jahrb. f. Min.*, 1885, 1, Ref., 16).—The amalgam occurs as a moss-like mass in nests in the quartz of the Friedrichsegen vein. Three assays gave: 42.47, 42.80, and 44.9 per cent. of mercury. In addition to silver, 0.06 per cent. of copper was found. This composition corresponds with the formula  $\text{Ag}_{12}\text{Hg}_5$ . Sp. gr. 12.703. Very ductile, and acquires, under the hammer, a metallic lustre. On heating, a porous mass of silver remains in the form of the original mineral. B. H. B.

**Crystallised Copper from Schneeberg.** By H. V. FOULLON (*Jahrb. f. Min.*, 1885, 1, Ref., 23).—Numerous small crystals of native copper occur planted on quartz at Schneeberg in Saxony. They are crystallised only in octahedra. Simple crystals are rare, twin crystals are more frequent, and groups of four most frequent. The forms usually unite by a face of the octahedron. B. H. B.

**Siegburgite.** By H. KLINGER and R. PITSCHEK (*Ber.*, 17, 2742—2746).—The physical properties of this fossil resin have been described by v. Lasaulx (this Journal, 1875, 615). The amount of sand found by the authors is much higher than is stated by v. Lasaulx; the powdered resin dried over sulphuric acid yielded 72·07—72·42 per cent. ash. When siegburgite is slowly distilled, a light yellow mobile liquid first comes over, then a thick dark-coloured distillate, the mass in the flask first melting and then becoming solid, whilst finally a grey-black sandy residue remains. The distillate contains cinnamic acid and cinnamene, which may be separated by agitation with soda solution; the lower fractions were also found to contain toluene and a little benzene, whilst the fractions 120—140° and 150—360°, have not yet been examined.

On treating siegburgite with aqueous soda, very little cinnamic acid is extracted; alcohol, ether, and benzene take up a small quantity of a resinous and amorphous substance; chloroform extracts a resin whilst the concretions swell up, the sand settles to the bottom covered with a gelatinous mass, which probably is principally metacinnamene, as when dried and distilled, it yields a considerable quantity of cinnamene together with cinnamic acid. It appears from these results that siegburgite is a fossil storax. A. K. M.

**Hatchettine from Seraing.** By G. DEWALQUE (*Jahrb. f. Min.*, 1885, 1, Ref., 21).—The melting point of this mineral is not fixed; at about 54—58° it begins to melt, but does not become perfectly fluid until a temperature of 62—64° is reached. Its behaviour on cooling is quite similar. Crystallisation begins at 59°, and at 56·5—57° the whole mass becomes solid. Hatchettine is, therefore, probably not a simple substance but a mixture. B. H. B.

**Mineralogical Notes on the Environs of Pontgibaud.** By F. GONNARD (*Jahrb. f. Min.*, 1885, 1, Ref., 26).—The author gives a list of the numerous minerals occurring near Pontgibaud. In addition to the usual lead ores (galena, cerussite, anglesite, pyromorphite, mimetosite), the following are worthy of note:—Fluorspar in large crystals from Pontgibaud and Martinèche. Small crystals of bournonite, from the Roure Mine, with the forms  $0P$ ,  $P\infty$ ,  $\infty P\infty$ ,  $\frac{1}{2}P$ ,  $P\infty$ ,  $\infty P\infty$ ; larger crystals occur at Barbecot. Tetrahedrite from Pranal in large crystals, in which the usual forms  $\frac{202}{2}$ ,  $\frac{0}{2}$  predominate; the composition is as follows:—

S.	Sb.	Cu.	Fe.	Zn.	Ag.	Total.	Sp. gr.
24·35	22·30	23·56	6·53	2·34	19·03	98·11	5·04

**Zinkenite** (argentiferous) from Peschadoire, in which the percentages of antimony and lead (45 and 28 respectively) do not agree with the usual analyses. The chlorophyllite occurring near the town of Pontgibaud is described somewhat in detail. B. H. B.

**Pseudomorphs.** By E. DÖLL (*Jahrb. f. Min.*, 1885, 1, Ref., 18—21).—The author describes a new pseudomorph, and several rare pseudomorphs from new localities. The pseudomorphs described are the following:—1. Marcasite after blende from the talc-like nacrinite of Schönfeld near Schlaggenwald. 2. Iron pyrites after marcasite from Kapnik. 3. Blende after galena and barytes in the quartz-andesite of Nagyag. 4. Quartz and red hæmatite after garnet from Carinthia. 5. Talc after quartz and dolomite from Oker in the Harz.

B. H. B.

**Stibnite from Japan.** By J. A. KRENNER (*Jahrb. f. Min.*, 1885, 1, Ref., 6—10).—The complexity of form observed among Japanese stibnite crystals is very remarkable. Of the 45 planes known previous to the publication of Dana's memoir (Abstr., 1884, 22), 30 have been observed on these Japanese stibnites, and, in addition to these, 40 new planes were determined by Dana. Krenner has now introduced 10 new symbols, 7 of which are identical with those found by Dana. The three new planes are the following:  $\frac{1}{17}P$ ,  $\frac{3}{13}P$ ,  $\frac{5}{19}P$ .

B. H. B.

**A Crystal of Stibnite from Japan.** By A. BRUN (*Jahrb. f. Min.*, 1885, 1, Ref., 10—11).—The author has measured a crystal from the island of Shikoku. The following forms were observed:— $\infty P\infty$ ,  $\infty P\frac{2}{3}$ ,  $P$ ,  $\frac{4}{3}P\frac{2}{3}$ ,  $\frac{2}{3}P$ ,  $\frac{9}{10}P$ ,  $\frac{2}{3}P\frac{2}{3}$ .  $a : b : c = 0.99839 : 1 : 1.01127$ .

B. H. B.

**Japanese Minerals.** By WADA (*Jahrb. f. Min.*, 1885, 1, Ref., 11—13).—Iron pyrites occurs as cubes at Kiura, in the island of Kiu-shiu, as  $O \cdot \left[ \frac{\infty O 2}{2} \right]$  at Kiso in the province of Shinano, and as  $O \cdot \infty O \infty$  at Utesan in the province of Idsumo. Copper pyrites occurs as tetrahedra from the veins in the diabase or diabase-tufts of Ani, province of Ugo, accompanied by galena, blende, quartz, and the usual vein minerals. Stibnite occurs in crystalline schists, in veins 0.63 metre wide and filled with compact ore, in cavities in which are found the crystals described by Dana and Krenner. The locality given by Dana (Abstr., 1884, 22) is incorrect. It should be the stibnite mine of Ichinokawa, near Saijo, province Jyo, in the island of Shikoku. The author next describes a long and thick crystal of apatite from the granite of the Kympusan Mountain, in the province of Kai. It is weathered on the surface, and has a sp. gr. of 3.19. Splendid specimens of topaz occur in the pegmatite veins in the granite of Otani-yama, near the town of Kioto. The crystals are colourless, yellow, and greenish, and are of great size. One of average dimensions is 77 mm. long in the direction of the axis  $c$ , and 75 mm. and 120 mm. in the direction of  $a$  and  $b$ . The following forms were observed:— $\infty P$ ,  $\infty P\frac{2}{3}$ ,  $\infty P\infty$ ,  $0P$ ,  $P$ ,  $\frac{1}{2}P$ ,  $\frac{1}{3}P$ ,  $2P\infty$ ,  $P\infty$ ,  $\frac{2}{3}P\infty$ ,  $P\infty$ ,  $\frac{1}{3}P\infty$ . Similar crystals occur at Nakatsu-gama, province of

**Mino.** The author next describes tourmaline from four localities, three of which are in granite or gneiss, and the fourth specimen was brought to Tokio, with pale green beryl, from the second of the topaz deposits mentioned above. The first three are black, and the last is azure-blue. One locality of black tourmaline is the Kimpusan Mountain, where for centuries rock crystals have been worked. A second locality is the granite of the Kirishima-yama, province of Osumi, in the island of Kiu-Shiu. The third black tourmaline occurs with potassium-mica, and felspar, as a constituent of a pegmatite of the province of Hidachi. Garnet occurs in three localities; at Kuroyuwa, in the province of Etchui, as reddish-brown crystals,  $\infty O, 2O_2$ , with decomposed felspar and quartz; at Wada-mura, province of Shinano, reddish-brown to black crystals,  $\infty O, 2O_2$ , occur; and in the mica schist of Yamao-muro, province of Hidachi, brown icositetrahedrons,  $2O_2$ , with the characteristic striation are met with. Zeolites are found in the cavities of a diabase amygdaloid from Mase-mura, province of Echigo. Milk-white apophyllite, similar to the crystals of Punah, and colourless crystals ( $2O_2$ ) of analcime, on a radiated crust of natrolite, occur. From the first of the above-mentioned topaz localities, a number of potash felspars come, similar to those of Striegau.

B. H. B.

**Marmalite from Himmelfahrt Mine, Freiburg.** By J. D. BRUCE (*Chem. News*, 50, 220).—The specimen had the usual appearance of marmalite, but contained an exceptionally large quantity of antimony. Analysis gave:—

Zn.	Fe.	Cu.	Sb.	Mn.	S.	Insoluble residue.
50.82	14.52	2.35	1.14	trace	31.67	0.14 = 100.64

D. A. L.

**Twin Crystals of Zircon.** By FOOTE (*Jahrb. f. Min.*, 1885, 1, Ref., 15—16).—At Eganville, Renfrew County, Canada, small but distinct twin-crystals of zircon occur. They are formed exactly like the well-known rutile and tinstone twin-crystals. The twinning plane is here, also,  $P\infty$ .

B. H. B.

**Products of the Alteration of Pitchblende.** By H. v. FOULLON (*Jahrb. f. Min.*, 1885, 1, Ref., 21—23).—The author gives a detailed description of the crystallised pitchblende from Mitchell Co., North Carolina, and adds, for the sake of comparison, an account of the other occurrences of pitchblende and its alteration-products. The crystals examined consisted of cubes with subordinate octahedron. The crystals from Mitchell Co. are mostly pseudomorphs, frequently containing a core of pitchblende. The exterior is lemon-yellow, and consists of uranophane; beneath this is an orange-coloured layer of gummite. The gummite represents the first stage of the decomposition of pitchblende, uranophane the second. Both products are described by the author as independent minerals. The chemical composition of the unaltered pitchblende is:—

$U_3O_4$ .	PbO.	$Fe_2O_3$ .	Total.
95.49	3.83	1.09	100.41

Analyses of gummite and similar minerals are given in the annexed table:—1 and 2, orange-coloured exterior of crystals from Mitchell Co.; 3, gummite from Joachimsthal; 4 and 5 eliasite from Joachimsthal; 6, pittinite from Joachimsthal; 7, coracite from Lake Superior.

	1.	2.	3.	4.	5.	6.	7.
SiO <sub>2</sub> .....	5·02	5·03	4·26	4·92	5·01	5·00	4·35
PbO .....	—	5·51	—	5·04	4·44	2·51	5·36
UO <sub>3</sub> .....	74·67	74·92	72·00	63·38	63·76	68·45	59·30
Fe <sub>2</sub> O <sub>3</sub> .....	0·46	0·36	—	8·64	8·55	4·54	2·24
Mn <sub>2</sub> O <sub>3</sub> .....	—	—	0·05	1·92	1·84	—	—
Al <sub>2</sub> O <sub>3</sub> .....	—	—	—	—	—	—	0·90
MgO .....	—	—	—	0·85	0·82	0·55	—
BaO .....	1·06	1·06	—	—	—	—	—
CaO .....	3·38	3·01	6·00	4·54	4·36	2·27	14·44
H <sub>2</sub> O .....	9·80	9·91	14·75	10·24	9·41	10·06	4·64
P <sub>2</sub> O <sub>5</sub> .....	—	—	2·30	—	—	—	—
Bi <sub>2</sub> O <sub>3</sub> .....	—	—	—	—	—	2·67	—
CO <sub>2</sub> .....	—	—	—	—	—	—	7·47
Insoluble.....	—	—	—	—	—	3·20	—

In discussing these analyses, the author concludes that in Kersten's analyses of gummite (3) the lead oxide was overlooked, and that all these products of the alteration of pitchblende agree with gummite, and that the names eliasite, pittinite, and coracite should therefore be dropped. From analyses 1 and 2 the formula  $\text{RU}_3\text{SiO}_{12} + 6\text{H}_2\text{O}$  is calculated. This mineral is of an orange colour, is not amorphous but crystalline, has a hardness of 3, and a sp. gr. of 4·7—4·84.

Analyses of uranophane are also given. 8, 9, and 10 are lemon-yellow products of the alteration of pitchblende from Mitchell Co.; 11, uranophane from Kupferberg, in Silesia; 12, uranotile from Neustädtl, near Schneeberg.

	8.	9.	10.	11.	12.	13.
SiO <sub>2</sub> .....	13·24	13·24	13·47	17·08	13·78	13·02
UO <sub>3</sub> .....	65·78	55·96	64·36	53·33	66·75	63·93
Fe <sub>2</sub> O <sub>3</sub> .....	0·14	trace	0·47	—	} 0·51	{ 3·03
Al <sub>2</sub> O <sub>3</sub> .....	—	—	—	6·10		
MgO .....	—	—	—	1·46	—	—
CaO .....	7·10	7·00	7·49	5·07	5·27	5·13
H <sub>2</sub> O .....	13·05	13·17	13·32	15·11	12·67	14·55
P <sub>2</sub> O <sub>5</sub> .....	—	—	—	—	0·54	—
K <sub>2</sub> O .....	—	—	—	1·85	—	—

It is remarkable that, in this mineral, the lead oxide is absent. The author is of opinion that the name "uranotile" must be

dropped. The formula is, according to Boricky,  $\text{CaU}_3\text{Si}_3\text{O}_{16} + 9\text{H}_2\text{O}$ ; according to Rammelsberg,  $\text{Ca}_2\text{U}_6\text{Si}_5\text{O}_{30} + 15\text{H}_2\text{O}$ ; and according to Genth,  $\text{CaU}_3\text{Si}_2\text{O}_{11} + 6\text{H}_2\text{O}$ . B. H. B.

**Listwaenite from the Poroschnaja Mountain, near Nischne-Tagilsk.** By M. v. MIKLUCHO-MACLAY (*Jahrb. f. Min.*, 1885, 1, Mem., 69—73).—In Macpherson's account of the rocks from the Spanish province of Galicia, a description is given of a crystalline schist, locally known as *duelo*, which appears to correspond with a rock from the Ural, described by G. Rose as listwaenite. In order to test how far the analogy extends, the author examined a number of specimens in the Heidelberg collection, from the Poroschnaja Mountain, near Nische-Tagilsk in the Ural.

The examination of the specimens of listwaenite showed that the rock consists mainly of reddish-brown magnesium carbonate and greenish-white talc, with grains of chrome iron ore. The analysis of the carbonate gave the following results:—

$\text{MgCO}_3$ .	$\text{FeCO}_3$ .	$\text{CaCO}_3$ .	Total.
73·47	19·94	7·47	100·88

The carbonate, therefore, is a lime-breunnerite. The analysis of the talc gave the following results:—

$\text{SiO}_2$ .	$\text{FeO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ .	Total.
62·61	3·44	29·55	5·18	100·78

The Poroschnaja rock, like Macpherson's *duelo*, is free from quartz, but listwaenites from a number of localities in the Ural are described by Rose, as being rich in quartz. A comparison of the quartz-free listwaenite with the Galician *duelo*, shows that the two rocks are identical. For the Galician rock, therefore, the correct name would be quartz-free listwaenite. B. H. B.

**Accidental Formation of Cerussite Crystals on Roman Coins.** By A. LACROIX (*Jahrb. f. Min.*, 1885, 1, Ref., 27).—Cerussite was found on Roman copper coins from Algiers, containing 16·20 per cent. of lead and 3·97 per cent. of tin. The coins were cemented together by copper carbonate, and the geodes, formed between them, contained cerussite, small cubes of cuprite, with malachite and azurite. The author is of opinion that the cerussite was formed by the action of solutions which had taken up alkali carbonates from the masonry. B. H. B.

**Colemanite.** By G. v. RATH (*Jahrb. f. Min.*, 1885, 1, Mem., 77—78).—An analysis of colemanite (named after W. T. Coleman, of San Francisco, the founder of the borax industry in the Pacific States), gave the following results:—

$\text{B}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{H}_2\text{O}$ .	$\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ .	$\text{SiO}_2$ .
48·12	28·43	22·20	0·60	0·65

After subtracting the impurities, this gives:—

$B_2O_3$ .	$CaO$ .	$H_2O$ .	Total.
48·72	28·79	22·49	100·00

This corresponds very closely with the priceite from Curry County, Oregon.

The new crystals recently found in the neighbourhood of the Dry Lake are transparent and extraordinarily rich in planes, forming one of the finest monoclinic combinations known. The following forms were observed:  $-P$ ,  $P$ ,  $-3P$ ,  $-3P3$ ,  $2P$ ,  $2P2$ ,  $P\infty$ ,  $2P\infty$ ,  $2P\infty$ ,  $\infty P$ ,  $\infty P2$ ,  $\infty P\infty$ ,  $\infty P\infty$ ,  $0P$ . The sp. gr. is 2·417, and the hardness 5.

B. H. B.

**Fluorapatites.** By A. DITTE (*Compt. rend.*, **99**, 967—970).—The phosphoric acid in fluorapatites can be replaced by arsenic or vanadic acid, with formation of strictly analogous compounds.

Fluorarsenates are obtained by the same methods as the fluorophosphates, substituting a metallic arsenate or arsenic acid for the phosphate or phosphoric acid. Ammonium arsenate may be used instead of arsenic acid, but in this case a platinum crucible cannot be employed, since it is attacked by the free arsenic which is liberated. A porcelain crucible, however, is only very slightly corroded by the fused fluoride. The reactions which take place are strictly analogous to those which occur in the formation of fluorophosphates, and the apatite obtained is quite free from chlorine.

*Calcium fluorarsenate*,  $3Ca_3As_2O_8, CaF_2$ , forms brilliant transparent hexagonal prisms, terminated by hexagonal pyramids, the faces of which are striated parallel with the base. The crystals dissolve readily in dilute acids, especially on heating, and they are decomposed by sulphuric acid with evolution of hydrofluoric acid. Barium, strontium, and magnesium fluorarsenates, prepared in like manner, are very similar to the corresponding phosphorus compounds.

*Fluorvanadates* can be obtained by the same methods, but the yield is not so satisfactory. Better results are obtained by using an excess of calcium fluoride, but part of the vanadic acid is always converted into a soluble compound, which yields a yellow solution when the fused mass is treated with water. Moreover, any apatite which may be formed is decomposed by the fused salts, unless the fluoride is in excess. A very small quantity of undecomposed fluoride is sufficient to ensure the stability of calcium fluorvanadate. In the case of strontium, however, and still more in the cases of barium and magnesium, this does not hold good. If only a small proportion of fluoride is used, no fluorvanadate is obtained, whilst if the fluoride is in large excess, the vanadate is attacked and converted into a soluble compound.

*Calcium fluorvanadate*,  $3Ca_3V_2O_8, CaF_2$ , forms thin white hexagonal needles, with hexagonal terminations. It can also be obtained by fusing 1 molecular proportion of vanadic acid with 3 of calcium oxide, and then fusing the calcium vanadate thus formed with a large excess of potassium chloride and a small quantity of fluorspar, for 15—20 hours.

*Strontium fluorvanadate* is obtained by the first methods in very small quantity, and intimately mixed with strontium vanadate. No barium or magnesium fluorvanadate could be obtained. C. H. B.

**Artificial Gypsum Crystals.** By A. LACROIX (*J. Pharm.* [5], 9, 111—113).—Small monoclinic prisms of gypsum, about 2 mm. long, were formed in a Brüner's lead pan, which had been out of use for about four months. When last used, a little water had been placed in the pan and thrown out again, so that a paste of undecomposed fluor-spar and some calcium sulphate remained. The pan had not been exposed to a temperature greater than 12° C. At the end of the four months, the little liquid left in the pan when last used had completely evaporated, and a beautiful incrustation of crystals had formed over the fluoride, and the sides of the pan. Their composition agreed closely with that required by  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ .

The crystals bore a striking resemblance in form to those obtained from the salt deposits of Bex (Canton Vaud), Switzerland.

J. T.

**A New Hydrous Manganese Aluminium Sulphate from Sevier Co., Tennessee.** By W. G. BROWN (*Amer. Chem. J.*, 6, 97—101).—This mineral and its locality are mentioned by Dana under kalinite. The mass analysed contained in cavities small silky needles, apparently monoclinic;  $\text{H.} = 1.5$ ; sp. gr. = 1.78. Analysis shows that this mineral is not kalinite, but is related to apjohnite and more nearly to bosjemanite (Dana), and the author suggests that these two minerals may perhaps be identical. The analytical results obtained were—

$\text{Al}_2\text{O}_3$ .	$\text{MnO}$ .	$\text{FeO}$ .	$\text{MgO}$ .	$(\text{CoNi})\text{O}$ .	$\text{CuO}$ .	$\text{SO}_3$ .	$\text{H}_2\text{O}$ .	Insoluble.
10.03	8.73	0.39	0.30	0.30	0.02	35.47	44.78	0.06 = 100.08

H. B.

**Occurrence of Linarite in Slag.** By P. DUDGEON (*Min. Mag.*, 5, 33).—Well-formed crystals of linarite, 3 mm. long, were found in some of the cavities in slag from an old lead-smelting place, evidently of Roman origin, on the farm of Martingarh, in the parish of Troqueer, in Scotland. There were no other crystallised minerals in the cavities.

B. H. B.

**Wulfenite from Beaujolais.** By A. LACROIX (*Jahrb. f. Min.*, 1885, 1, Ref., 27).—Wulfenite is found in numerous places near the abandoned mines of Beaujolais, especially abundantly at Monsols. It is generally accompanied by pyromorphite. The crystals are tabular, and the colour varies from orange-yellow to deep red. In the latter crystals, however, no trace of chromium could be found, to the presence of which Fournet ascribed this colouring. The author is of opinion that the colour is due to long exposure to the atmosphere. [Groth and Jost (*Zeits. f. Kryst.*, 7, 592) have already shown that the presence of chromium is not the cause of the colour of wulfenite, and Ochsensius (*ibid.*, 7, 593) found that red wulfenite crystals become lighter on exposure to air and light.]

B. H. B.

**Amphibole from the Aranyer Mountain.** By A. FRANZENAU (*Jahrb. f. Min.*, 1885, 1, Ref., 17—18).—Up to the present time, 18 planes have been observed in amphibole crystals; of these, 14 have been detected on the Aranyer crystals. In addition to these, the



author has added the following five new planes:  $\infty P\bar{2}$ ,  $-2P\bar{\infty}$ ,  $-\frac{2}{3}P\bar{\infty}$ ,  $-5P\bar{5}$ ,  $-\frac{1}{2}P$ .  $a : b : c = 0.54812 : 1 : 0.29455$ .  $\beta = 74^\circ 39.7'$ . The crystals are of a green colour, and occur in a reddish trachyte. Twin crystals were not observed. B. H. B.

**An American Locality for Helvine.** By H. C. LEWIS (*Jahrb. f. Min.*, 1885, 1, Ref., 15).—Helvine occurs in orthoclase in the mica mine near Amelia Court House, Virginia, in sulphur-yellow crystalline masses along with topazolite.  $H. = 6$ ; sp. gr. = 4.306; lustre, resinous; partially translucent; fusible. An analysis of the raw material (I) is given, together with the results without the mother-rock impurities (II).

	SiO <sub>2</sub> .	BeO.	MnO.	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.
I.	23.10	11.47	45.38	2.05	2.68	0.64	0.39
II.	25.48	12.63	39.07	2.26	2.95	0.71	0.43

	Na <sub>2</sub> O.	S.	Mn.	Rock.	Total.
I.	0.92	4.50	—	9.22	100.35
II.	1.01	4.96	8.66	—	95.16

The substance is decomposed by hydrochloric acid. The mineral has without doubt much in common with helvine, but the composition is very different, for helvine contains about 32.5 per cent. of silica. The sp. gr., too, is different, that of helvine being but 3.2. Further investigation is therefore necessary, more especially as to the purity of the material. B. H. B.

**Hyalophane from Jakobsberg.** By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1885, 1, Ref., 26).—Hyalophane occurs at Jakobsberg, Wernmland, Sweden, in slaty beds in limestone containing haussmannite and manganese epidote. The principal mass is white, but in the middle occur reddish, and at the edges, bluish-green spathic masses. The latter gave on analysis the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	BaO.	MgO.	MnO.	Alkalis.	Total.
53.53	23.33	7.30	3.23	trace	11.71	99.10

The absence of rubidium and caesium was proved. This variety differs in composition from the red variety from Jakobsberg, and from the variety found in Binnenthal, in Wallis. B. H. B.

**Garnet (var. Spessartite) from Amelia Co., Virginia.** By C. M. BRADBURY (*Chem. News*, 50, 220).—The specimen is from the mica mines of Amelia Co.; it is of a pale pink to flesh colour, resembling rhodonite more than the usual form of garnet. Its hardness is 6.5, its sp. gr. 4.20. From the following results, it will be seen that the manganese is higher, whilst the iron and aluminium are lower than usual:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	OH <sub>2</sub> .
36.34	12.63	4.57	44.20	1.49	0.47	trace = 99.70

D. A. L.  
r 2

**Kaslinite from Calhoun Co., Alabama.** By G. H. ROWAN (*Chem. News*, **50**, 220).—The specimen is unusually pure, and comes from near Jacksonville. It is white with a creamy tinge, earthy with clayey odour, adheres to the tongue, and is slightly greasy to the touch. Its sp. gr. = 1·688. The following are the results of its analysis:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	MgO, Fe <sub>2</sub> O <sub>3</sub> .	
45·77	39·45	0·79	13·96	trace	= 99·97
D. A. L.					

**Infusorial Earth from Richmond, Virginia.** By J. M. CABELL (*Chem. News*, **50**, 219).—As previous analyses of this substance have apparently been made on impure specimens, a specimen was procured composed almost exclusively of distinguishable infusoria. It is white with a tinge of yellow, is slightly harsh to the touch, and has a sp. gr. of 2·321. The results of analysis are appended:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Nitrogenous matter (N × 6).	OH <sub>2</sub> .	Total.
75·68	9·88	2·92	0·29	0·69	0·02	0·08	0·84	8·37	= 98·77

The water and silica were made up in the following manner:—

Silica dissolved by boiling 1 hour with 20 per cent. soda.	29·60
„ „ „ 2 hours „ „ „	4·79
„ undissolved „ „ „	41·29
	<hr/>
	75·68
Loss by drying over H <sub>2</sub> SO <sub>4</sub> .....	3·37
Loss at 100° .....	1·17
Loss by ignition (less N) .....	3·83
	<hr/>
Water .....	8·37
	D. A. L.

**Description of a Crystal of Euclase.** By M. GUYOT (*Min. Mag.*, **5**, 107—108).—The crystal comes from the mining district Boa Vista, near Villa Ricca, Brazil, where alluvial strata containing diamonds occur with chlorite schist. The weight of the crystal is 15·45 grams; sp. gr. 3·087. It is 35 mm. long, sea-green like beryl, with vitreous lustre, nacreous on the cleavage planes. One termination is perfectly developed, the other fractured. The prism ∞P gave the angle 144° 37'. The following planes were present:—∞P∞, ∞P∞, 0P, ∞P, ∞P2, 3P3, 3P3, 2P2. The crystal is one of the finest crystals of euclase which has ever been discovered.

B. H. B.

**Variety of Chloropal from Albemarle Co., Virginia.** By L. N. CHAPPELL (*Chem. News*, **50**, 219—220).—The mineral is found in leaf-like pieces of various sizes in a ferruginous clay; the neigh-

bouring rock is largely composed of quartz, felspar, and epidote. When dug out, it is massive and soft; when dry it becomes harder and brittle with earthy fracture. It can be cut with a knife, giving a slightly lustrous surface, greasy to the touch. It does not adhere to the tongue, and is of a light yellowish-green colour. Its hardness is about 1; its sp. gr. = 2.06. When treated with hydrochloric or sulphuric acid, it is decomposed with separation of silica. Its composition is—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	OH <sub>2</sub> .	Total.
38.64	20.05	22.18	0.04	1.09	0.44	15.71	= 98.15

which nearly corresponds to that of pinguite, a variety of chloropal,  
 $2\text{Al}_2\text{O}_3, 3\text{SiO}_2 + 4\frac{1}{2}\text{H}_2\text{O}$ . D. A. L.

**Orthite from Virginia.** By G. A. KÖNIG (*Jahrb. f. Min.*, 1885, 1, Ref., 14).—In the mica mine near Amelia Court House, Virginia, two specimens of orthite were found. They were pitch-black and hard, but covered with a thin reddish-brown incrustation. Sp. gr. 3.368. The mineral fuses with intumescence to a black slag, and is decomposed by concentrated hydrochloric acid and dilute sulphuric acid. The analyses gave—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CeO <sub>2</sub> .	La <sub>2</sub> O <sub>3</sub> + Di <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.
32.90	17.80	1.20	8.00	14.20	10.04	11.32
		MnO.	H <sub>2</sub> O.	Total.		
		1.00	3.20	99.66		

together with a trace of uranium, but neither yttrium nor beryllium.  
 B. H. B.

**Variety of Saponite.** By J. J. DOBBIE (*Min. Mag.*, 5, 131—132).—The variety of saponite described is of a deep chocolate-brown colour. It was obtained from the dolerite of the Cathkin Hills, near Glasgow. It occurs in irregular lenticular patches, or in horizontal veins. It has a conchoidal fracture and soapy feel. H. = 2. Sp. gr. 2.214. The analyses gave the following results:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	CO <sub>2</sub> .	H <sub>2</sub> O.	Total.
I.	40.07	6.61	4.16	8.69	2.67	19.24	0.38	17.16	98.98
II.	39.90	6.94	3.75	8.91	2.32	19.28	0.40	17.28	98.78
III.	40.81	6.77	4.28	8.73	2.09	19.76	0.36	17.11	99.91

At 100°, 13.02 per cent. of water is given off. The Cathkin Hills mineral differs from other saponites in containing a larger percentage of ferrous oxide, and a smaller percentage of total water.

B. H. B.

**Relation between the Optical Properties and Chemical Composition of Pyroxene.** By C. DOELTER (*Jahrb. f. Min.*, 1885, 1, Mem., 43—68).—The admixture of  $\text{FeCaSi}_2\text{O}_6$  with the silicate  $\text{CaMgSi}_2\text{O}_6$ , causes an increase in the value of the extinction angle in the plane of symmetry, and in the prism faces. In the same way, this increase is brought about by the admixture of silicates of the

formula  $R''R'''_2\text{SiO}_6$ , and the same amount per cent. of the latter silicate effects a greater alteration in the extinction angle than is effected by  $\text{CaFeSi}_2\text{O}_6$ . If the sums of all these silicates ( $\text{CaFeSi}_2\text{O}_6$  and  $R''R'''_2\text{SiO}_6$ ) be taken as abscissæ, and the values of the extinction angles be taken as ordinates, the curve obtained is  $y = a + bx + cx^2$ . If, however, for abscissæ the values of  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  (together or separately) are taken, a less regular curve is obtained. The curve for the diopsides (combinations of  $\text{CaMgSi}_2\text{O}_6$  and  $\text{CaFeSi}_2\text{O}_6$ ) does not coincide with that for the alumina augites. For the lime-magnesia silicate, theoretically perfectly free from iron and alumina, the extinction angle is about  $32^\circ 30'$ . The value of the angle formed by the perpendicular to the orthopinacoid and an optic axis, increases, as a rule, in proportion to the total amount of the iron and aluminium silicates present.

B. H. B.

**New Mineral from Godemas.** By LODIN (*Jahrb. f. Min.*, 1885, 1, Ref., 28).—At Godemas (Hautes-Alpes), two ore veins occur in the masses of finely-granular muscovite granite, stratified conformably to the gneiss beds. One vein contains quartz, iron pyrites, copper pyrites, blende, and a little argentiferous galena; the other contains quartz, blende, and antimonial fahlerz, rich in silver. The analysis of the mass filling the second vein gave the following results:—

$\text{SiO}_2$ .	S.	Sb.	As.	Cu.	Fe.	Zn.	Pb.	Ag.	Total.
66.31	9.93	3.85	0.15	5.98	2.09	8.67	0.80	0.15	97.93

From the same vein, the author obtained a compact, homogeneous mineral of a dark bluish-grey colour and fibrous texture, with sp. gr. 6.17. It fuses at a dull red heat, and gives grains resembling the original mineral. The composition is as follows:—

$\text{SiO}_2$ .	S.	Sb.	As.	Cu.	Fe.	Pb.	Ag.	Total.
0.25	17.54	0.62	trace	44.52	0.79	35.87	0.11	99.70

This corresponds to the formula  $2\text{CuS} + \text{PbS}$ . As the mineral contains but little antimony and silver, although the vein-mass is comparatively rich in these metals, the author is of opinion that it was formed by the action of the fahlerz on the galena, poor in silver.

B. H. B.

**Nepheline Rocks in the United States.** By J. E. WOLFF (*Jahrb. f. Min.*, 1885, 1, Mem., 69).—The author collected in the Crazy Mountains, Montana, peculiar eruptive rocks, which in veins and masses penetrate the horizontal sandstone and conglomerate of the Cretaceous formation. These rocks consist of nepheline, a mineral of the sodalite group, augite, magnesia mica, olivine, magnetite, apatite, and the usual accessory constituents. These eruptive masses, therefore, belong to the nepheline rocks, a class hitherto undiscovered in the United States.

B. H. B.

**Meteorite from Durango.** By L. HÄPKE (*Jahrb. f. Min.*, 1885, 1, Ref., 32—33).—In the autumn of 1882, a new meteoric iron was found near Durango, in Mexico, at a depth of 25 to 30 cm. From

the slight depth, it was concluded that the meteorite had reached that spot during the year 1882. The iron has a prismatic-pyramidal shape, and weighs 46 kilos. Sp. gr. 7·74—7·89. The analysis gave the following results :—

Fe.	Ni.	Co.	P and C.
91·78	8·35	0·01	traces

The meteorite has been purchased by the British Museum.

B. H. B.

**Meteoric Sand.** By F. MAUGINI (*Gazzetta*, 14, 130—136).—The peculiar glowing appearance of the sky at dawn and twilight observed during the winter months of 1883–1884, was attributed by some to particular atmospheric conditions, such as general stillness, and an extraordinary quantity of aqueous vapour diffused at high elevations; but by others to the volcanic dust of the Krakatoa eruption. Yung, in Geneva, and Nordenskiöld, in Stockholm, have observed the presence of iron in meteoric dust which fell on snow. On the 16th and 19th February, and March 10th, 1884, the author collected some red-coloured dust at Reggio, in Calabria, which, when examined under the microscope, seemed to consist of mica, quartz, and irregular polyhedral crystals. The glowing phenomenon, accompanied by rain, was observed on these dates. An incomplete analysis of this dust, when freed from organic matter, gave the following results :—

Magnetic iron oxide .....	6·4
Insoluble in acids .....	38·75
Soluble in acids .....	54·85

The insoluble portion contained sulphuric and phosphoric acids, silica, calcium, magnesium, arsenious and ferric oxides; and the soluble portion, aluminium, nickel, and manganous oxides. This dust differs from that obtained at Stockholm, in containing no cobalt and only traces of nickel. The dust was not derived from Etna, for the direction of the wind on the days in question was opposite to that in which Etna and Reggio are situated; and further, the volcanic ashes of Etna are black. It also differed from dust carried from the deserts of Sahara by the sirocco in containing iron (see Abstr., 1884, 165), so it would appear to be of peculiar origin.

V. H. V.

**Mineral Water of Salies-du-Salat.** By P. SABATIER (*Bull. Soc. Chim.*, 42, 98—99).—The following results were obtained on analysis of the mineral water of Salies-du-Salat (in the department of Haute-Garonne), the outflow of which has been known for several centuries :—

1 kilogram of the water contains—	Grams.
Sodium chloride .....	31·494
Potassium chloride .....	0·5165
Sodium sulphate .....	0·4924
Calcium sulphate .....	2·6785
Magnesium sulphate .....	0·5592
Calcium carbonate .....	0·3136
Sodium silicate .....	0·0096

There were also found traces of bromine and iodine, nitric and boric acids, together with aluminium, lithium, strontium, iron, manganese, and zinc. As these results are not in accordance with the analyses of Bories and Filhol, it is probable that there are irregular or periodic variations in the composition of the spring.

V. H. V.

**Water from the Red Spring of Zacaune (Tarn, France).** By L. SOUBEIRAN and G. MASSOL (*Jour. Pharm.* [5], 9, 85—89).—This ferruginous spring rises on the flank of a mountain composed of talcose schist of the transition period.

1020 c.c. of the water gave 38 c.c. of gas containing  $\text{CO}_2 = 6$  c.c.,  $\text{O} = 5$  c.c., and  $\text{N} = 27$  c.c. A slight effervescence at the spring results entirely from the disengagement of nitrogen. The water was found to contain—in grams per litre:—

$\text{FeCO}_3 \dots$	0.026	$\text{Na}_2\text{CO}_3 \dots$	0.033	$\text{SiO}_2 \dots\dots\dots$	0.031
$\text{CaCO}_3 \dots$	0.052	$\text{NaCl} \dots\dots$	0.001	Organic matter	traces
$\text{MgCO}_3 \dots$	0.013	$\text{Na}_2\text{SO}_4 \dots$	traces	Total....	0.156

A deposit formed by the spring consists mainly of iron oxide and silica; it moreover contains magnesia and lime, and effervesces with acid.

J. T.

**Arsenic in Mineral Waters.** By J. LEFORT (*Jour. Pharm.* [5], 9, 81—85).—In all analyses of mineral waters, the arsenic is represented as being in the higher state of oxidation, as arsenates, and not as arsenites. The author recommends the well-known reactions with hydrogen sulphide, in slightly acidified solutions, as sufficient to determine the question. It is quite possible that arsenic may occur in natural water as arsenate if the mineralisation of the water has taken place under oxidising conditions; but if under reducing conditions, then arsenites would be produced.

J. T.

### Organic Chemistry.

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**The Hydrocarbon,  $C_8H_{14}$ , prepared from Allyl Diethyl Carbinol.** By S. REFORMATSKY (*J. pr. Chem.* [2], **30**, 217—224).—The hydrocarbon,  $C_8H_{14}$ , is obtained by heating allyl diethyl carbinol with sulphuric acid; this reaction yields a liquid boiling at 120—140°, from which, by a method similar to that employed in the purification of the hydrocarbon  $C_{10}H_{18}$  (Abstr., 1883, 1073), the hydrocarbon is obtained as a colourless liquid, insoluble in water, but easily soluble in alcohol, ether, and benzene, and boiling at 122—123°. It is oxidised by exposure to the air, forming the compound  $C_8H_{14}O_2$ . Its sp. gr. at 0° is 0.7734, and at 15.4° 0.7588 (water at 0° = 1), at 15.4° 0.7595 (water at 20° = 1), and 0.75856 (water at 4° = 1), at 18° is

0.7572 (water at  $20^{\circ} = 1$ ), and calculated for water at  $4^{\circ}$  as unit, it is 0.75662. Its vapour-density is 3.81. The determination of its refractive index gave the following results, which are not in accord with the rule laid down by Brühl:—

	P.	t.	$d_{\frac{t}{4}}$	$n_{\alpha}$	$n_D$	$n_{\beta}$	$n_{\gamma}$
1....	110	$18^{\circ}$	0.75662	1.44171	1.44477	1.45386	1.46143
2....	110	$15.4^{\circ}$	0.75856	1.44340	1.44687	1.45577	—

	A.	B.	$\frac{n_{\alpha} - 1}{d}$	$P\left(\frac{n_{\alpha} - 1}{d}\right)$	$R_{\alpha}$	Diff.
1 .....	1.426975	0.63546	0.5841	64.25	58.2	6.05
2 .....	1.42839	0.64696	0.5845	64.29	58.2	6.09

	$\frac{A - 1}{d}$	$P\left(\frac{A - 1}{d}\right)$	$R_A$	Difference.
1 .....	0.5646	62.11	56.94	5.17
2 .....	0.5647	62.12	56.94	5.18

Bromine unites with this hydrocarbon to form a heavy thick oily liquid. When oxidised, the hydrocarbon yields chiefly propionic and acetic acids, together with a small quantity of formic acid.

If the constitution of this hydrocarbon is represented by the formula  $C_2H_4 : CEt.C_3H_5$ , the formation of these acids is easily explained.

P. P. B.

**A Reddish Coloration of Cyanide Solutions.** By L. HABEL (*Ber.*, **17**, 2840—2841).—A reddish coloration has been frequently observed on adding potassium cyanide to cuprammonium solution, but the cause of it is unknown to the author.

A. K. M.

**Hydroferrocyanic Acid and its Derivatives.** By A. ÉTARD and G. BÉMONT (*Compt. rend.*, **99**, 972—975 and 1024—1026).—The product of the action of hydrochloric acid on a concentrated solution of potassium ferrocyanide in presence of ether is not, as is commonly stated, hydroferrocyanic acid, but a compound of this acid with ether,  $H_4FeCy_6.2Et_2O$ . This compound is also obtained when dry ether is added to crystals of anhydrous hydroferrocyanic acid obtained by slow evaporation. It slowly loses its ether when exposed to the air, and if the compound is treated with sodium hydroxide the ether is at once liberated, and can thus be recovered perfectly free from alcohol.

When dry hydroferrocyanic acid is heated at  $440^{\circ}$  (in sulphur



vapour), it loses only 46 per cent. of hydrocyanic acid, and yields a chamois-coloured crystalline residue of hydro-diferrous pentacyanide, (1)  $\text{Fe}(\text{CN})_5\text{FeH}$ .

If ammonium ferrocyanide is heated at  $440^\circ$  until the product has a constant composition, it loses 62.4 per cent. of water and hydrocyanic acid, and a homogeneous insoluble compound is obtained of the composition  $\text{Fe}(\text{CN})_5\text{FeNH}_4$ . This is the ammonium salt of the preceding compound. On further heating, it is decomposed into nitrogen, ammonium cyanide, and a dense black carbide of iron,  $\text{FeC}_2$ .

When hydroferrocyanic acid is boiled with water in a vacuum, it loses hydrocyanic acid, and yields a dense crystalline citron-coloured compound, (2)  $\text{FeCy}_6\text{FeH}_2 + 2\text{H}_2\text{O}$ , which is the acid corresponding with Williamson's salt,  $\text{FeCy}_6\text{FeK}_2$ .

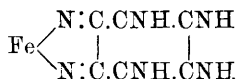
If the boiling with water is effected in presence of air, instead of in a vacuum, a dark blue precipitate is obtained; this, however, is not Prussian blue, but has the formula (3)  $n(\text{FeC}_2\text{N}_2\text{H}_2\text{O})$ . From its behaviour with potassium hydroxide it seems to be a hydrated ferrosiferrous ferrocyanide.

If hydroferrocyanic acid is boiled with ammonium chloride and water in a vacuum, a sulphur-yellow crystalline powder is obtained, which, when dried out of contact with air, has the composition (4)  $\text{FeCy}_6\text{FeNH}_4\text{H} + 3\text{H}_2\text{O}$ .

If this compound is exposed to moist air, or if the original boiling is effected in presence of air, it is oxidised to a dark blue compound, (5)  $(\text{FeCy}_6)_2\text{Fe}_2(\text{NH}_4)_2 + 6\text{H}_2\text{O}$ .

When this salt is heated at  $440^\circ$ , it loses water and ammonium cyanide, and yields the insoluble cyanide, (6)  $(\text{FeCy}_6)_2\text{Fe}_2$ , corresponding with (1).

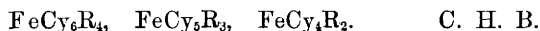
These reactions are easily understood if it is assumed that hydroferrocyanic acid is a tetrabasic non-saturated acid with the constitution



The compounds (1), (6), &c., for example, differ from the corresponding ferrocyanides by at least  $\text{CNR}'$ .

*Nitroprussides* may be classified with the pentacyanides (1), (6), &c., described above. When sodium nitroprusside is heated at  $440^\circ$  in a vacuum, in an apparatus arranged as if for an estimation of nitrogen by Dumas' method, it reaches a limit of dissociation when it has lost 29.9 per cent. by weight. The decomposition is represented by the equation  $\text{FeCy}_5\text{Na}_2\text{NO} + 2\text{H}_2\text{O} = \text{FeCy}_4\text{Na}_2 + \text{NO} + \text{CN} + 2\text{H}_2\text{O}$ . The three gaseous products, however, react on one another with formation of black compounds. Ferroso-sodium tetracyanide,  $\text{FeNa}_2\text{Cy}_4$ , is a chamois-coloured crystalline compound which is scarcely altered at a dull red heat, but loses a little cyanogen at bright redness. It is insoluble in, and is not decomposed by, water.

It is evident that the compounds formed by the union of metallic cyanides furnish at least three definite and distinct types, viz.:—



**Derivatives of Cyanethine.** By C. RIESS (*J. pr. Chem.* [2], 30, 145—171).—*Monobromocyanethine*,  $C_9H_{14}BrN_3$ , is prepared by heating bromine and a solution of cyanethine hydrobromide in sealed tubes at  $80-100^\circ$ ; the product of the reaction is *monobromocyanethine hydrobromide*, from which the free base is obtained by decomposition with ammonia. It crystallises in small needles, is sparingly soluble in water, and easily soluble in alcohol, ether, and chloroform; it melts at  $153^\circ$ . Monobromocyanethine is a base forming salts which are soluble in water and alcohol, and easily obtained in well-defined crystals. The hydrochloride forms a sparingly soluble compound with mercuric chloride, an *aurochloride*,  $C_9H_{14}BrN_3 \cdot HAuCl_4$ , crystallising in yellow shining needles, and a *platinochloride*,  $(C_9H_{14}BrN_3)_2 \cdot H_2PtCl_6$ , crystallising in rhombic octahedrons.

*Ethoxycyanethine*,  $C_9H_{14}N_3 \cdot OEt$ , is obtained by heating monobromocyanethine with an alcoholic solution of sodium ethylate; the base is extracted from the product of the reaction by ether, from which it separates on evaporation as a solid mass consisting of rhombic leaflets. It melts at  $115^\circ$ , commences to sublime even at  $100^\circ$ , and can be distilled unchanged at over  $300^\circ$ ; it is soluble in cold water, forming an alkaline solution, from which when heated the base separates as an oil; this solution precipitates copper and lead salts as hydroxides. The base is easily soluble in alcohol, ether, chloroform, and acids. Its salts are easily soluble in alcohol and water, and crystallise well; it forms crystalline double salts with silver, platinum, and gold salts. Mercuric chloride produces a white precipitate in solutions of the hydrochloride; when heated, this melts to form an oil.

*Ethoxyhydroxycyanconine*,  $C_9H_{12}(OEt)N_2 \cdot OH$ , is formed by treating the above compound, dissolved in glacial acetic acid, with nitrous acid. From ether, it separates as a radiated crystalline mass, melting at  $51^\circ$ ; it exhibits great resemblance to ethoxycyanethine, its aqueous solutions have a neutral reaction, and with silver nitrate give a white precipitate of the compound  $C_9H_{11}Ag(OEt)N_2 \cdot OH$ . When ethoxycyanethine is heated with concentrated hydrochloric acid in sealed tubes at  $180-200^\circ$ , a compound is produced which is apparently the dihydroxy-base  $C_9H_{12}N_2(OH)_2$ . It crystallises from ether in needles melting at  $151^\circ$ ; its aqueous solution has a neutral reaction. The nitrate gives with silver nitrate a precipitate of the compound  $C_9H_{12}AgN_2(OH)_2 + H_2O$ . The hydrochloride forms a yellow oily compound with gold chloride. With chlorine-water and bromine-water, its aqueous solutions give white precipitates of polychlorides and polybromides respectively.

*Methoxycyanethine*,  $C_9H_{14}N_3 \cdot OMe + H_2O$ , is obtained from monobromocyanethine by acting on it with sodium methylate. It crystallises from ether in rhombic crystals, which effloresce, and melt at  $130^\circ$ . It exhibits a great resemblance to the ethoxycyanethine, and like it is converted into a hydroxy-base,  $C_9H_{12}(OMe)N_2 \cdot OH$ , when treated with nitrous acid.

*Monobromohydroxycyanconine*,  $C_9H_{12}BrN_2 \cdot OH$ , is obtained by heating monobromocyanethine with hydrochloric acid in sealed tubes at  $200^\circ$ . It is identical with that obtained by E. v. Meyer

(Abstr., 1883, 353) by the action of nitrous acid on monobromocyanethine.

*Auclidocyanethine*,  $C_9H_{14}N_3.NHPh$ , is formed, together with aniline-hydrobromide, by heating monobromocyanethine with aniline in sealed tubes at  $200-230^\circ$ . It is insoluble in water, and slightly soluble in alcohol, from which it crystallises in groups of shining leaflets melting at  $125^\circ$ . It is a base easily soluble in acids, from which sodic hydroxide and ammonia precipitate it. Bromocyanethine, when carefully fused with zinc ammonium chloride, yields a base, probably  $C_9H_{14}(NH_2)N_3$ . Potassium cyanide converts the monobromo-compound into cyanethine.

*Tribromocyanethine*,  $C_9H_{12}Br_3N_3$ . In the presence of water, the action of bromine on cyanethine produces chiefly monobromo-together with a small quantity of tribromo-cyanethine. When a solution of cyanethine and chloroform is heated with bromine in sealed tubes at  $100^\circ$ , the latter compound is formed; it crystallises from alcohol in lustrous rhombic leaflets melting at  $126^\circ$ . It is easily soluble in ether and chloroform, but insoluble in water, and is soluble in strong acids, the salts formed being decomposed by water. The anurochloride forms yellow, lustrous, silky needles.

*Tribromohydroxycyanconine*,  $C_9H_{10}Br_3N_2.OH$ , is formed by treating the tribromo-compound with nitrous acid; it melts at  $149^\circ$ , crystallises in white needles, insoluble in water, and resembles the monobromohydroxy-base.

*Trichlorocyanethine*,  $C_9H_{12}Cl_3N_3$ , is obtained by the action of chlorine on a solution of cyanethine in chloroform; the residue obtained after evaporating the chloroform solution is dissolved in absolute alcohol, and on addition of water yields the trichloro-compound in lustrous, pearly, rhombic leaflets, melting at  $110^\circ$ . This compound resembles the tribromo-derivative, and like it is converted by the action of nitrous acid into a hydroxy-base,  $C_9H_{10}Cl_3N_2.OH$ , which crystallises in needles melting at  $132^\circ$ .

An alcoholic solution of sodium ethylate converts trichlorocyanethine into a brown oil, probably the triethoxy-base.

*Triamidocyanethine* seems to be produced by the action of alcoholic ammonia on trichlorocyanethine in sealed tubes at  $130^\circ$ . It is a base and forms the platinochloride  $[C_9H_{12}(NH_2)_3N_3]_2.H_2PtCl_6$ .

*Tetrachlorocyanconine*,  $C_9H_{10}Cl_3N_2Cl$ , is formed by the action of phosphorus pentachloride on the trichlorohydroxy-base. It is an oil; when treated with concentrated sulphuric acid, it is reconverted into this same hydroxy-base.

Hydroxycyanconine is formed by the action of hydriodic acid on the trichlorohydroxy-base.

*Moniodocyanethine*,  $C_9H_{14}IN_3$ , is formed when a solution of cyanethine in dilute sulphuric acid, heated on a water-bath, is treated with nitric acid until all iodine disappears. On adding caustic soda, the compound is precipitated in small white needles. The base is easily soluble in acids and caustic alkalis, and melts at  $152^\circ$ . It forms an aurochloride,  $(C_9H_{14}IN_3).HAuCl_4$ , which crystallises from alcohol in orange-yellow leaflets.

*Moniodohydroxycyanconine*,  $C_9H_{12}IN_2.OH$ , is formed by the action of

fuming nitric acid on the iodo-base dissolved in glacial acetic acid. It is soluble in acids and alkalis, water, and ordinary solvents; it crystallises in aggregates of needles, resembling the corresponding bromo-derivative, and melts at  $157^{\circ}$ . By the further action of nitric acid hydroxycyanconine is obtained (*loc. cit.*) P. P. B.

**Action of Allyl and Isobutyl Iodides on Zinc and Acetone.** By E. SCHATZKY (*J. pr. Chem.* [2], 30, 216—217).—These bodies react on one another, producing allyl dimethyl carbinol and a small quantity of a liquid of the composition  $C_{10}H_{20}O$ , boiling at  $192$ — $196^{\circ}$ . This compound the author regards as isobutylallyl dimethyl carbinol, a homologue of the bye-product obtained by Dieff in the preparation of allyl dimethyl carbinol (Abstr., 1883, 1076).

P. P. B.

**Composition of a Bye-product obtained in the Preparation of Diallyl Carbinol.** By W. SCHESTAKOFF (*J. pr. Chem.* [2], 30, 215).—This substance, which has the composition  $C_{10}H_{18}O$ , is probably analogous to that obtained by Dieff (Abstr., 1883, 1076) in the preparation of dimethyl carbinol; it may be regarded as propyl diallyl carbinol.

P. P. B.

**Derivatives of Symmetrical Isodichlorethyl Ether (Ethylidene Chloride).** By A. GEUTHER (*Annalen*, 226, 223—231).—Laatsch has lately shown (Abstr., 1883, 788) that the substance known as ethylidene oxychloride has the formula  $O(CHClMe)_2$ ; the present paper describes derivatives prepared from it by double decomposition with metallic salts of organic acids.

The *acetate*,  $O(CHMe.O\overline{Ac})_2$ , a colourless liquid of faint ethereal odour, boils at  $191$ — $193^{\circ}$ , has sp. gr.  $1.071$  at  $16^{\circ}$ , and  $1.067$  at  $20^{\circ}$ . When agitated for a long time with cold water, it is decomposed into aldehyde and acetic acid. It is not decomposed by aqueous sodium carbonate in the cold; on heating, aldehyde resin separates. The *propionate*,  $O(CHMe.C_3H_5O_2)_2$ , a colourless liquid of faint ethereal odour, boils at  $210$ — $215^{\circ}$ , and has a sp. gr. of  $1.027$  at  $26^{\circ}$ . The *butyrate*,  $C_{12}H_{22}O_5$ , a colourless liquid of sp. gr.  $0.994$  at  $20^{\circ}$ , boils at  $235$ — $240^{\circ}$ , and does not seem to be decomposed by water. The *formate*,  $C_6H_{10}O_5$ , is a colourless liquid of penetrating odour; it boils at  $175$ — $185^{\circ}$  with partial decomposition, and has a sp. gr. of  $1.314$  at  $21^{\circ}$ . When heated at  $150^{\circ}$  in sealed tubes, it is decomposed with separation of a brown resin and formation of carbonic oxide, formic acid, and aldehyde. The *benzoate*,  $C_{18}H_{18}O_5$ , crystallises in slender, colourless needles. The *succinate*,  $C_8H_{12}O_5$ , is a colourless viscid substance, sparingly soluble in water, but readily soluble in very dilute aqueous soda.

Attempts to prepare a mixed acetate and butyrate were not successful. When the acetate is heated with butyric anhydride at  $180$ — $190^{\circ}$ , in sealed tubes, the butyrate and acetic anhydride are formed; the reverse reaction could not be effected.

A. J. G.

**Optical Inactivity of Cellulose and the Rotatory Power of Pyroxylin.** By A. BÉCHAMP (*Compt. rend.*, 99, 1027—1029).—The

author criticises Levallois' paper (Abstr., 1884, 1288), and gives a *résumé* of his own earlier researches (*Compt. rend.*, **42**, 1210, and **51**, 255). According to his results, insoluble cellulose and the soluble cellulose obtained by the action of sulphuric acid, are both optically inactive. Prolonged action of various reagents, such as sulphuric or hydrochloric acid, however, converts the cellulose into substances having a high dextrorotatory power, but these substances can be completely converted into dextrose. Many specimens of pyroxylin are optically inactive, but others have a dextrorotatory power which varies considerably with different samples. The cellulose obtained by reducing these pyroxylin is optically inactive. It would seem, therefore, that any rotatory power possessed by derivatives of cellulose is due to some molecular transformation resulting from the action of the reagents employed.

C. H. B.

**Grevillea Gum.** By G. FLEURY (*Jour. Pharm.* [5], **9**, 479—480).—An exudation occurs frequently upon the trunk of the *Grevillea robusta* (Proteaceæ), similar in appearance to the gum of the cherry tree. The author has examined a product from Algeria. It is yellowish-red, slightly translucent, and slightly friable. In water it swells a little, and slowly produces a very persistent white emulsion, which passes through all filters. It contains no starch, but gives 3 per cent. of ash, principally calcium carbonate, with a little potash. The emulsion treated with absolute alcohol gives a copious precipitate of gum proper. When the alcoholic solution is evaporated, it gives 5.6 per cent. of a reddish transparent resin, with slightly acid properties; this is soluble in alkalis and carbon bisulphide. The gum proper is grey; does not appear to give a true solution in water, the liquid being turbid and viscous; it gives no precipitate with ferric chloride. The gum already soaked in water, dissolves immediately if a little potash lime, or potassium carbonate be added, and the solution gelatinises under the influence of a ferric salt. This characteristic reaction distinguishes this product from all other known gums. The gum is lævorotary, and has no action on Fehling's solution. Lead acetate gives a white precipitate, copper sulphate a blue gelatinous one. Nitric acid converts it into mucic acid, mixed with a little oxalic acid. Dilute sulphuric acid after long boiling produces a sugar similar to that obtained from Senegal gum.

J. T.

**Ethenylamidoxime and its Derivatives.** By E. NORDMANN (*Ber.*, **17**, 2746—2756).—In continuation of Tiemann and Krüger's work (Abstr., 1884, 734 and 1325), the author has studied the compound obtained by the action of hydroxylamine on acetonitrile.

*Ethenylamidoxime*,  $C_2H_6N_2O$ , was obtained by acting on acetonitrile with hydroxylamine. The *hydrochloride*,  $C_2H_6N_2O \cdot HCl$ , forms glistening, white, hygroscopic scales which melt at  $140^\circ$ , and are very stable when pure. Care must, however, be taken during the process of purification to avoid the presence of free hydrochloric acid, as otherwise much decomposition takes place. The hydrochloride is easily soluble in water and alcohol, insoluble in ether, chloroform, &c. The free base is very unstable, and is best prepared by the addition of the calculated quantity of sodium ethylate to a dilute alcoholic solution of

the hydrochloride, separation of the sodium chloride by the addition of ether, and evaporation of the solution at the ordinary temperature under reduced pressure. Even then, slight decomposition always takes place. The free base crystallises in long colourless and odourless needles, which melt at  $135^{\circ}$ , and are stable in dry air. It is insoluble in benzene, ether, and chloroform, easily soluble in alcohol and water, and the aqueous solution gives a deep-red coloration with ferric chloride. It is more easily decomposed by heat than the analogous benzenylamidoxime, but resembles the latter in its properties and reactions. Its constitution is probably  $\text{NH}_2.\text{CMe}:\text{NOH}$ . It possesses both basic and acid properties. The sulphate is very hygroscopic, and scarcely crystallisable; the alkali salts are very unstable. The free base is decomposed by water, more readily by acids, into acetamide and hydroxylamine,  $\text{NH}_2.\text{CMe}:\text{NOH} + \text{H}_2\text{O} = \text{NH}_2.\text{OH} + \text{NH}_2.\text{CMe}$ . Sodium nitrite decomposes the hydrochloride thus:  $\text{NH}_2.\text{CMe}:\text{NOH} + \text{HNO}_2 = \text{NH}_2.\text{CMe} + \text{N}_2\text{O} + \text{H}_2\text{O}$ , but there appears always to be a small quantity of a very volatile substance formed, which the author thinks is perhaps diethenylazoxime,  $\text{CMe} \begin{smallmatrix} \text{N.O} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{CMe}$ . The *methyl* and *ethyl* ethers of ethenylamidoxime are very unstable, hygroscopic compounds. *Ethenylamidoxime benzyl ether*,  $\text{NH}_2.\text{CMe}:\text{NO}.\text{C}_6\text{H}_5$ , is obtained by adding the calculated quantity of sodium ethylate to a solution of the hydrochloride in absolute alcohol, and then digesting with benzyl chloride. It forms a pale yellow oil, which cannot be distilled even in a vacuum, and at the ordinary pressure decomposes at  $200^{\circ}$ . Benzaldehyde and ammonia are amongst the products of decomposition. The ether is almost insoluble in water, easily soluble in alcohol, ether, &c. This ether is much more stable towards acids than ethenylamidoxime, and has lost the acid properties of the latter. The hydrochloride forms small white flakes which melt at  $163^{\circ}$ , and yields a platinochloride crystallising in brownish-red prisms.

When ethenylamidoxime is gently warmed with aniline *ethenylanilidoxime*,  $\text{NHPh}.\text{CMe}:\text{NOH}$ , is formed. It is very stable, forms large brownish-yellow flakes and melts at  $121^{\circ}$ . It is soluble in alcohol, ether, benzene, and boiling water, almost insoluble in cold water. It forms acid and basic salts, and yields a crystalline platinochloride. An alcoholic solution, when treated with ferric chloride, turns deep violet, and with excess of the reagent olive-green: when the solution is heated, both colours change to reddish-brown.

When ethenylamidoxime hydrochloride is heated with benzoic chloride, *ethenylazoximebenzenyl*,  $\text{N} \begin{smallmatrix} \text{CMe} \\ \diagup \quad \diagdown \\ \text{O.CPh} \end{smallmatrix} \text{N}$ , is formed. This compound forms long white needles, melts at  $57^{\circ}$  to an oil which distils readily in a current of steam, and begins to sublime at  $70$ – $80^{\circ}$ . It is soluble in alcohol, ether, and benzene, insoluble in water. It is isomeric with Tiemann and Krüger's benzenylazoximethenyl, melting at  $41^{\circ}$ , and is similar to it in properties.

When ethenylamidoxime is heated with acetic anhydride, a yellow syrup is obtained, which probably contains diethenylazoxime, but the author has not yet succeeded in isolating the latter compound.

*Propenylamidoxime* is formed by the action of hydroxylamine on propionitrile, and is now undergoing investigation. L. T. T.

**Trioxymethylene.** By L. PRATESI (*Gazzetta*, **14**, 139—141).—The formula  $(C_2HO)_3$  generally assigned to the polymeride of methaldehyde is based on its conversion of hydrogen sulphide into the corresponding sulphur compound thiomethaldehyde, whose composition is shown to be  $(C_2HS)_3$  from a determination of its vapour-density and the composition of its crystalline compounds with silver nitrate. This argument cannot, however, be considered final, for ethaldehyde, under similar conditions, is converted not into its sulphur analogue, but into a substance easily transformed into parathioethaldehyde  $(C_2H_4S)_3$ .

In order to throw some light upon this question, the author has heated oxymethylene in sealed tubes, with a trace of sulphuric acid, in such a way that the resultant material can sublime in a cool part of the tube. A sublimate is formed which, when resublimed, can be obtained in long flexible crystals 10 cm. in length; they are very difficult to pulverise, have the irritating odour of methaldehyde, and sublime slowly at ordinary temperatures. They melt at  $60^\circ$  and are soluble in water, alcohol, and ether, the solutions reducing ammoniacal solutions of silver nitrate in presence of potash. Vapour-density determinations gave results corresponding with the formula  $(CH_2O)_3$ . This substance may be designated  $\alpha$ -trioxymethylene. It is proposed to carry on investigations regarding the transformations of this substance.

V. H. V.

**Action of Hydrocyanic Acid and of Dilute Sulphuric Acid on Aldol.** By C. A. LOBRY DE BRUYN (*Bull. Soc. Chim.*, **42**, 161—166).—A slightly acid solution of potassium cyanide was mixed with an ethereal solution of aldol in the proportion of 1.5 molecular proportion of cyanide to 1 of aldol, sufficient hydrochloric acid added to decompose the cyanide, and the liquid allowed to remain two hours. The ethereal solution was then removed and evaporated, the syrupy residue treated with water two or three times to remove unaltered aldol, and the product dried over calcium chloride. In this way, a colourless liquid is obtained, containing 6.5 per cent. of nitrogen, a result agreeing with the formula  $(C_4H_5O_2)_2, HCN$ . The same compound is obtained when one and the same quantity of aldol is subjected to four successive treatments with nascent hydrocyanic acid. When this compound is boiled with concentrated barium hydroxide solution, a salt is formed which could not be obtained pure. Analysis showed, however, that its composition more nearly approaches that of an acid containing  $C_6$  than  $C_5$ . Other salts were obtained, but they are very unstable, and do not crystallise.

When 1 vol. of aldol is mixed with 2 vols. of pure liquid hydrocyanic acid, and the mixture allowed to remain, a heavy oily liquid separates and finally crystallises in small needles. When these needles are purified by washing, drying, and recrystallising from ether, they melt at  $113$ — $114^\circ$ , have the composition  $C_8H_{14}O_3$ , and are identical with the isodialdane described by Wurtz. Liquid

hydrocyanic acid, therefore, acts towards aldol as a dehydrating agent.

If aldol is mixed with about six times its weight of sulphuric acid of sp. gr. 1.32, a flocculent precipitate gradually forms, very soluble in alcohol and ether. This precipitate is a mixture of  $C_3H_{14}O_3$  ( $2C_4H_8O_2 - H_2O$ ) and  $C_{12}H_{20}O_4$  ( $3C_4H_8O_2 - 2H_2O$ ) in proportions varying with the conditions. When the solution from which these flocculent precipitates have separated is exhausted with ether, the ethereal solution evaporated, and the product dried in a vacuum, the compound  $C_{12}H_{20}O_4$  is obtained as a colourless liquid.

The facts that 2 mols. of aldol combine with only 1 mol. of hydrocyanic acid, and that the aldol forms isodialdane in contact with liquid hydrocyanic acid, would seem to indicate that the aldol has undergone condensation with formation of dialdol.

C. H. B.

**Some New Sulpho-derivatives of the Fatty Acids.** By J. M. LOVÉN (*Ber.*, 17, 2817—2825).—*Thiodiglycollic acid* is readily obtained by the action of sodium sulphide on sodium monochloracetate, both in concentrated solution; the product is acidulated with sulphuric acid and extracted with ether. The properties of the acid so obtained agree with those of the thiodiglycollic acid prepared by Schulze (*Zeit. f. Chem.*, 1865, 73), Schreiber (this Journal, 1876, ii, 398), and Andreasch (*Abstr.*, 1880, 236). The lead salt has the formula  $S(CH_2.COO)_2Pb$ . When thiodiglycollic acid is neutralised with an alkaline carbonate and a 5 per cent. solution of potassium permanganate gradually added, heat is developed, whilst *sulphonediacetic acid*,  $SO_2(CH_2.COOH)_2$ , is produced; this crystallises in rhombic plates melting at  $182^\circ$ , is very readily soluble in water and alcohol, less so in ether. When it is heated to about  $200^\circ$ , it decomposes into carbonic anhydride and dimethylsulphone. The barium salt,  $SO_2(CH_2.COO)_2Ba + 5H_2O$ , readily parts with 4 mols.  $H_2O$ , but it cannot be obtained anhydrous, heat decomposing it with formation of dimethylsulphone. *Ethyl sulphonediacetate*,  $SO_2(CH_2.COOEt)_2$ , forms a thick oil, nearly insoluble in water, and is decomposed by distillation; it yields a voluminous amorphous precipitate,  $SO_2(CHNa.COOEt)_2$ , with sodium ethylate, and is converted by aqueous ammonia into the *amide*,  $SO_2(CH_2.CONH_2)_2$ . Sulphonediacetamide forms lustrous scales, sparingly soluble in cold, readily in hot water; it turns brown at  $220^\circ$  without fusing. *Sulphonedipropionic acid*,  $SO(C_2H_4.COOH)_2$ , obtained by the oxidation of thiodilactylic acid (*Abstr.*, 1884, 1298), crystallises in four-sided plates, melts at  $155$ — $156^\circ$ , and is extremely soluble in water, alcohol, and ether. It may also be prepared by the action of methyl iodide on ethyl sulphonediacetate and sodium ethylate. *Sulphonedibutyric acid*,  $SO_2(C_3H_7.COOH)_2$ , may be obtained by heating together ethyl sulphonediacetate (1 mol.), sodium ethylate (2 mols.), and ethyl iodide (2 mols.) at  $120$ — $130^\circ$ , and saponifying the ether produced by baryta-water; it crystallises in well formed octahedra melting at  $152^\circ$ . When the product of the action of methyl iodide on ethyl sulphonediacetate and sodium ethylate described above is treated in the same way with a second quantity of sodium ethylate and methyl iodide, and the product decomposed by means of hot



baryta-water, barium sulphonediiisobutyrate,  $\text{SO}_2(\text{C}_3\text{H}_5\text{COO})_2\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$ , is obtained; it forms vitreous needles, sparingly soluble in cold, moderately in hot water. The free acid melts at  $188^\circ$ .

A. K. M.

**$\beta$ -Dipropylacrylic Acid.** By A. ALBITZKY (*J. pr. Chem.* [2], 30, 209—212).—This acid is obtained from  $\beta$ -dipropylethylenelactic acid by acting on it with phosphorus pentachloride or sulphuric acid; the crude acid is purified by conversion into its zinc and other salts. It forms a hard white crystalline mass, is soluble in alcohol, ether, and benzene, and crystallises from the latter in needles melting at  $80$ — $81^\circ$ . Its constitution is expressed by the formula  $\text{CPr}_2\text{:CH.COOH}$ .

The *sodium* and *potassium* salts are easily soluble non-crystalline substances, the *lithium* salt crystallises from alcohol in rounded masses, and has the composition  $\text{C}_9\text{H}_{15}\text{O}_2\text{Li} + 2\text{H}_2\text{O}$ . The *calcium* and *barium* salts are sparingly soluble in water, crystallising from alcohol with 1 mol.  $\text{H}_2\text{O}$ . The *zinc* salt is insoluble in water and alcohol. The *copper* and *lead* salts are both insoluble in cold water, but soluble in hot water, the latter crystallises from alcohol in bundles of needles containing  $2\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ . The *silver* salt is insoluble in water.

P. P. B.

**Propenylglycollic Acid.** By C. A. LOBRY DE BRUVN (*Bull. Soc. Chim.*, 42, 159—161).—When crotonaldehyde is mixed with aqueous hydrocyanic acid in the cold, no reaction takes place even after several weeks, but if the mixture is heated in a sealed tube at  $70$ — $80^\circ$  for about 10 days, the crotonaldehyde disappears and the liquid becomes somewhat brown. The liquid product is placed in a vacuum for several days to remove the excess of hydrocyanic acid, and is then mixed with moderately strong hydrochloric acid, no attempt being made to isolate the cyanhydrin. The ammonium chloride which formed is separated after some days, the liquid diluted with water, extracted with ether, and the ethereal solution evaporated, when a brown strongly acid liquid is obtained, miscible with water. If this liquid is dissolved in water, neutralised with baryta, and concentrated, it yields a white crystalline salt, which, after being purified by repeated recrystallisation, has the composition  $\text{Ba}(\text{C}_5\text{H}_7\text{O}_3)_2$ . According to its method of formation, this acid will have the constitution  $\text{CH}_3\text{CH:CH.CH(OH).COOH}$ , and may be called propenylglycollic acid, a name which is preferable to that of angelactic acid, proposed by Bischoff and Pinner (*Ber.*, 5, 212).

A solution of the acid or of its barium salt rapidly decolorises bromine-water.

When the aqueous solution of the acid is neutralised with baryta, and the barium salt allowed to crystallise, the mother-liquor has an acid reaction, and if it is again neutralised and still further concentrated, the acid reaction reappears. These facts point to the existence of an internal anhydride. The last mother-liquor, when concentrated first on a water-bath, and finally over sulphuric acid, yields a solid amorphous residue, which is probably a salt of a poly-acid.

C. H. B.

**Formation of the Anhydrides of Mono- and Di-basic Acids.**

By R. ANSCHÜTZ (*Annalen*, **226**, 1—13).—The anhydrides of mono-basic acids can be prepared by heating for several hours a mixture of the acid chloride with the acid; for example, acetic chloride and acetic acid, benzoic chloride and benzoic acid, &c. The yield varies from 50 to 90 per cent. of the theoretical. Better results are obtained by the action of a dibasic acid on the corresponding chloride.

Möller (*J. pr. Chem.* [2], **22**, 194) has recently shown that an almost theoretical yield of succinic anhydride is obtained by heating equivalent quantities of succinic chloride and succinic acid, and then distilling the product.

Attempts to prepare a mixed anhydride by acting on benzoic acid with acetic chloride were unsuccessful.

A large number of anhydrides of dibasic carboxylic acids have been obtained by the author and others, by the action of acetic chloride on the dibasic carboxylic acids, namely, the anhydrides of succinic, monochloro-succinic, monobromo-succinic, maleic, acetomalic, di-aceto-tartaric, diaceto-racemic, citraconic, and itaconic, camphoric, phthalic, and diphenic acids.

In preparing the anhydrides of succinic, camphoric, phthalic, and diphenic acids, the acetic chloride may with advantage be replaced by acetic anhydride.

W. C. W.

**Racemic Acid from Fumaric Acid and the Calcium Salts of the Four Isomeric Tartaric Acids.** By R. ANSCHÜTZ (*Annalen*, **226**, 191—201).—Kekulé and the author have shown (*Abstr.*, 1881, 156) that the racemic acid obtained by the oxidation of fumaric acid, is crystallographically identical with the racemic acid prepared from dextrotartaric acid. Proof of its chemical identity is now given by showing that its sodium ammonium salt, like that of ordinary racemic acid, can be resolved into a mixture of the salts of dextrotartaric and lævotartaric acids. The salts of these latter acids were identified both by chemical and crystallographical examination.

Calcium racemate always crystallises with 4 mols.  $H_2O$  in microscopic needle-shaped prisms. Crystals suited for measurement could not be obtained. Calcium mesotartrate,  $C_4H_4O_6Ca + 3H_2O$ , was prepared from inactive tartaric acids derived from the three sources, namely, from dextrotartaric acid, from dibromosuccinic acid, and from maleic acid. The three preparations were found to be crystallographically and optically identical. It crystallises in the triclinic system; axial ratios:  $a : b : c = 0.886 : 1 : 0.96764$ ; observed faces:  $\infty P_\infty$ ,  $\infty \bar{P}_\infty$ ,  $\bar{P}'_\infty$ ,  $P'_\infty$ ,  $\infty P'_1$ ,  $\infty \bar{P}'_1$ ,  $\infty P'_2$ ,  $\infty \bar{P}'_2$ .

Calcium dextrotartrate,  $C_4H_4O_6Ca + 4H_2O$ , and calcium lævotartrate,  $C_4H_4O_6Ca + 4H_2O$ , crystallise in identical forms and do not show hemihedric faces. They crystallise in the rhombic system; axial ratios:  $a : b : c = 0.87157 : 1 : 0.90834$ ; observed faces,  $P_\infty$ ,  $\bar{P}_\infty$ .

A. J. G.

**Ethylidenethenyltricarboxylic Acid.** By E. HJELT (*Ber.*, **17**, 2833—2835).—The triethyl salt of this acid is readily obtained by the action of ethyl sodomalonate on ethylic  $\alpha$ -chlorocrotonate. It boils

at 285—287°. The free acid,  $\text{CHMe}:\text{C}(\text{COOH})\cdot\text{CH}(\text{COOH})_3$ , is moderately soluble in water, more sparingly in ether, and melts at 185° with evolution of carbonic anhydride. The barium and calcium salts dissolve readily in cold, less so in hot water; the silver salt,  $\text{C}_7\text{H}_5\text{O}_6\text{Ag}_3$ , forms a flocculent precipitate. The monethyl-derivative,  $\text{C}_9\text{H}_{12}\text{O}_6 + 3\text{H}_2\text{O}$ , obtained by saponifying the normal salt with a slight excess of alkali and crystallising the oily product from water, forms large well-formed crystals melting at 70°. When placed in a desiccator this loses 2 mols.  $\text{H}_2\text{O}$ , and the residual compound  $\text{C}_9\text{H}_{12}\text{O}_6 + \text{H}_2\text{O}$  melts at 145°.

A. K. M.

**Ethyl Acetylenetetracarboxylate.** By C. A. BISCHOFF and C. RACH (*Ber.*, 17, 2781—2788).—This ether, prepared by the action of iodine on ethyl monosodomalonate, melts at 76°. When sufficient sodium is employed to form the disodium-derivative, *ethyl dicarbon-tetracarboxylate*,  $\text{C}_2(\text{COOEt})_4$  (Conrad and Guthzeit, *Abstr.*, 1884, 297) is formed. This crystallises in short thick hexagonal prisms melting at 56°. When two atomic proportions of sodium are dissolved in the smallest possible quantity of alcohol, and then added to ethyl malonate, *ethyl disodomalonate* is precipitated. This is quickly filtered and washed with ether, and then forms a white powder, but the authors were never able to obtain it quite pure, as slow decomposition at once sets in. If the precipitate first formed is not filtered off, it is very soon redissolved, and the addition of ether then precipitates a much more stable white powder, which gives numbers agreeing with the formula  $\text{COONa}.\text{CHNa}.\text{COOEt}$ . Ethyl propenyltricarboxylate yields a similar compound,  $\text{COONa}.\text{CNa}(\text{COOEt}).\text{CHMe}.\text{COOH}$ . Attempts to obtain the salt,  $\text{CH}(\text{COOEt})_2.\text{C}(\text{COOEt})_2.\text{CH}(\text{COOEt})_2$ , by the action of sodium ethylate on a mixture of ethyl malonate and ethyl chloromalonate, proved unsuccessful. *Ethyl acetylenetetracarboxylate*,  $\text{CEt}(\text{COOEt})_2.\text{CH}(\text{COOEt})_2$ , was obtained by acting on ethyl sodethylmalonate with ethyl chloromalonate. It forms a viscid colourless oil which boils at about 200° under 150 mm. pressure. When treated with chlorine at 70—80°, it forms the *mono-chloro-derivative*, an oil possessing an irritating odour and a sp. gr. of 1.076 at 20° compared with water at 15°. Unlike most monosubstituted malonic derivatives, ethyl acetylenetetracarboxylate does not form chloro-derivatives. If the temperature is raised to 200°, regular absorption of chlorine takes place, but carbonic anhydride is given off, and *ethyl dichlorethenyltricarboxylate* is formed. An attempt to obtain ethyl dichloroacetylenetetracarboxylate by the action of iodine on ethyl sodochloromalonate proved also unsuccessful. The iodine solution was at once decolorised, but after a time, iodine was again liberated and ethyl dicarbon-tetracarboxylate formed. The authors have found that the chlorine in ethyl chloromalonate is capable of liberating iodine from sodium iodide, and it is probable that in the above reaction the compound wished for was first produced, but then decomposed by the sodium iodide formed.

L. T. T.

**Monobromo- and Dibromo-pyromucic Acids.** By F. CANZONERI and V. OLIVERI (*Gazzetta*, 14, 172—180).—Schiff and Tassinari

have described two isomeric monobromopyromucic acids prepared by the action of potash on the addition-product of bromine on ethyl pyromucate, and fractional crystallisation from boiling water. In this paper, a description is given of a repetition of these experiments, boiling benzene being used as the fractionating menstruum. The crude product of the above reaction was by this means separated into a monobromo-pyromucic acid melting at  $155^{\circ}$ , identical with one of the acids described by Schiff, and a dibromopyromucic acid melting at  $185^{\circ}$ , identical with an acid described by Tonnies.

A better method for their separation is based on the different degrees of solubility of their barium salts in cold water, in which that of the former is readily, but that of the latter sparingly soluble. It would thus appear probable that by the limited action of bromine on pyromucic acid there is produced, besides the dibromide, a certain quantity of the tetrabromide of pyromucic acid; the former yields the monobromo-, the latter the dibromo-substituted acid. *Monobromopyromucic acid* crystallises in clinorhombic prisms soluble in alcohol and ether, its *barium* salt in quadrilateral scales; its silver salt is an amorphous precipitate. *Dibromopyromucic acid* crystallises in hexagonal laminæ soluble in ether and alcohol, sparingly soluble in water; its *barium* salt in prismatic needles; its *silver* salt is a white amorphous powder. Experiments were made on the dry distillation of the ammonium salts of these acids with a view of obtaining pyrroline from them, but, owing to the small quantity of material, the results were far from satisfactory.

V. H. V.

**Action of Hydrogen on Acetamide.** By J. C. ESSNER (*Bull. Soc. Chim.*, **42**, 98).—Acetamide, when treated with sodium amalgam in the presence of sodium bicarbonate, is converted into alcohol and sodium acetate. With the copper-zinc couple, it yields alcohol, together with small quantities of aldehyde, and an oil decomposing on distillation. The simultaneous formation of alcohol and aldehyde may be expressed by the following equations:— $\text{C}_2\text{H}_3\text{O.NH}_2 + 2\text{H}_2 = \text{NH}_3 + \text{C}_2\text{H}_5\text{O}$  and  $\text{C}_2\text{H}_3\text{O.NH}_2 + \text{H}_2 = \text{NH}_3 + \text{C}_2\text{H}_4\text{O}$ . The evolution of ammonia was very marked.

V. H. V.

**Occurrence of Leucine and Tyrosine in Beet Molasses.** By E. O. v. LIPPMANN (*Ber.*, **17**, 2835—2840).—A considerable quantity of the alcoholic liquors employed in treating lime sucrate by the elution method, was neutralised with sulphuric acid, and after remaining for some time the solution was separated from the precipitate. The liquor was then freed from alcohol and evaporated to a small bulk, but no further separation took place. On dissolving the product in hot water and adding lead acetate, an abundant precipitate was produced. This was filtered off, the solution treated with hydrogen sulphide, concentrated to a syrup, and introduced into alcohol, which produced a sticky tough precipitate, probably containing dextran. The alcoholic solution was evaporated, treated with lead acetate and with animal charcoal, and on evaporating the filtrate and allowing it to remain for a time, crystals were

obtained, the first crop of which consisted of *tyrosine*, and the second a mixture of tyrosine with *leucine*, the latter being readily separated by crystallisation from alcohol. The specific rotatory powers of the tyrosine and leucine so obtained were found to agree with those of animal tyrosine and of leucine obtained from casein, with which they are no doubt identical.

A. K. M.

**Derivatives of Carbamide.** By R. BEHREND (*Ber.*, **17**, 2846—2847).—The author recently described a compound obtained by the union of carbamide with ethyl acetoacetate (*Abstr.*, 1884, 583). When the sodium salt,  $C_5H_7N_2O_3Na$ , of this compound (*loc. cit.*) is decomposed by acids, a molecule of water is eliminated, and a substance,  $C_5H_6N_2O_2$ , formed. When this is treated with nitric acid, the methyl-group is oxidised to carboxyl, and a nitro-group introduced; a dibasic acid is obtained, the hydrogen potassium salt,  $C_5H_2N_3O_6K + H_2O$ , of which can be split up into carbonic anhydride and the potassium salt of a new nitro-compound,  $C_4H_3N_3O_4$ . When reduced, this yields a base which combines with cyanic acid to form a compound  $C_5H_6N_4O_3$ ; this is distinguished from xanthine by containing in addition the elements of a molecule of water, but it readily yields the murexide reaction. The investigation is being continued.

A. K. M.

**Action of Hydroxylamine on Pyrroline.** By G. L. CIAMICIAN and M. DENNSTEDT (*Gazzetta*, **14**, 156—157).—On boiling an alcoholic solution of equal parts of hydroxylamine hydrochloride, sodium carbonate, and pyrroline, there is formed, besides ammonium carbonate, a white crystalline substance,  $C_4H_5N_2O_2$ , melting at  $173^\circ$ . The reaction may provisionally be represented thus:— $C_4H_4NH + 2(NH_2.OH) = C_4H_4(NH.OH)_2 + NH_3$ ; but the authors propose to examine the reaction more completely, and to extend their investigations to other imido-compounds.

V. H. V.

**Pyrroline  $\alpha$ -Carboxylic Acid.** By G. L. CIAMICIAN and P. SILBER (*Gazzetta*, **14**, 162—173).—On heating together a mixture of pyrroline, ammonium carbonate, and water in sealed tubes at  $130$ — $140^\circ$ ,  $\alpha$ -pyrrolinecarboxylic acid,  $C_4H_4N.COOH$ , is formed, identical with that obtained by Schwanert from ammonium pyromucate (*Abstr.*, 1882, 212). The reaction is however very incomplete, a large proportion of pyrroline remaining unaltered. If the reaction be effected above  $140^\circ$ , a small quantity of an acid is produced probably identical with  $\beta$ -pyrrolinecarboxylic acid. The *calcium salt* of the  $\alpha$ -acid forms sparingly soluble white scales of the composition  $C_{10}H_8N_2O_4Ca$ ; when perfectly dry, it yields pyrroline on distillation. The *silver salt*, obtained by the addition of silver nitrate to an aqueous solution of the barium salt, forms small needles, sparingly soluble in water; the *methyl salt*, formed by the action of methyl iodide on the silver salt, crystallises in long needles or large prisms having an aromatic odour. It melts at  $73^\circ$ , is readily soluble in ether and in alcohol, sparingly soluble in water. The *ethyl salt*, obtained in a similar manner, melts at  $39^\circ$ , boils at

230—232°, is readily soluble in alcohol, ether, and petroleum, but only sparingly in water. If the vapour of bromine is passed into a boiling aqueous solution of methyl  $\alpha$ -pyrrolinecarboxylate, a white flocculent precipitate is formed: this is a tribromo-derivative,  $C_4Br_3NH.COOMe$ , which crystallises in long needles melting at 209°, and is readily soluble in ether and boiling alcohol, sparingly in water. Thus  $\alpha$ -pyrrolinecarboxylic acid differs in its reaction with bromine from pyromucic acid, which forms an additive-product containing 4 atoms of bromine. The  $\alpha$ -tribromopyrrolinecarboxylic acid crystallises in long needles soluble in ether, alcohol, and acetone; when heated at 140—150° it is completely decomposed without fusion. By the action of acetic chloride on silver  $\alpha$ -pyrrolinecarboxylate, an *acetyl-derivative* is obtained; this forms scales which melt at 75°, but are decomposed at the point of fusion into acetic acid and pyrocoll (Abstr., 1881, 295). The introduced acetyl-grouping may replace an atom of hydrogen in the imido- or carboxyl-group:— $C_4H_3N\overline{Ac}.COOH$  or  $C_4H_3NH\overline{COAc}$ . Either of these substances might be decomposed in accordance with the above change; the authors, however, consider the latter formula to be the more probable, inasmuch as their experiments tend to show that the hydrogen in the imido-group cannot be displaced by acetyl if a hydrogen-atom in the pyrroline nucleus is displaced by the acetyl- or carboxyl-group.

When methyl  $\alpha$ -pyrrolinecarboxylate is heated with excess of acetic anhydride in sealed tubes at 250—260°, the methyl salt of acetyl- $\alpha$ -pyrrolinecarboxylic acid,  $C_4H_2\overline{Ac}NH.COOMe$ , is formed, which crystallises in long needles melting at 113°, soluble in alcohol, ether, and boiling water. By the action of silver nitrate, a silver derivative,  $C_4H_2NO_2Ag$ , is obtained as a white precipitate. On saponifying the methyl salt and subsequently acidifying, the corresponding acid,  $C_4H_2\overline{Ac}NH.COOH$ , is obtained; this forms shining white leaflets melting at 186°, soluble in water, alcohol, and ether. Its silver salt,  $C_4H_2\overline{Ac}.NH.COOSAg$ , is a sparingly soluble precipitate; its *lead salt* forms glistening needles, and its *calcium salt*,  $(C_4H_2NO_3)_2Ca.7OH_2$ , forms large prisms belonging to the triclinic system. V. H. V.

**Synthesis of Furfurane-derivatives from Ethyl Diacetosuccinate.** By L. KNORR (*Ber.*, 17, 2863—2870).—Ethyl carbopyrotritartrate is formed when ethyl diacetosuccinate is heated at 200° or treated with concentrated hydrochloric acid, the product being identical with the compound  $C_{10}H_{12}O_8$  described by Harrow (*Trans.*, 1878, 433). It dissolves readily in alkalis and in sodium carbonate solution, acids reprecipitate it unchanged; it is saponified by boiling with aqueous or alcoholic potash or with dilute sulphuric acid, as stated by Harrow. By the action of concentrated sulphuric or phosphoric acid on ethyl diacetosuccinate in the cold, a molecule of water is eliminated and *diethyl carbopyrotritartrate*,  $C_{12}H_{16}O_8$ , is obtained, showing that carbopyrotritartric acid is a *dicarboxylic acid*. This diethyl-derivative has not the character of an ethyl salt of a ketonic acid, is insoluble in alkalis, and does not react with either phenylhydrazine or hydroxylamine. Its properties, mode of formation, and also the conversion of carbopyrotritartric acid into pyrotritartric acid indicate it to be

diethyl dimethylfurfuranedicarboxylate,  $O \begin{matrix} \swarrow \\ \text{CMe} : \text{C.COOEt} \\ \searrow \\ \text{CMe} : \text{C.COOEt} \end{matrix}$ , and carbo-

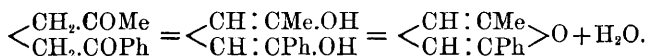
pyrotritaric acid is therefore *dimethylfurfuranedicarboxylic acid*. Diethyl dimethylfurfuranedicarboxylate boils at  $275.5^\circ$  (bar. 735 mm.). When ethyl carbopyrotritarate is warmed with an excess of alcoholic potash, the *normal potassium salt* is obtained, and by action of barium nitrate on this, the *barium salt*  $\text{C}_8\text{H}_6\text{BaO}_6$ . The acid liberated from the potassium salt forms slender white needles melting at  $230^\circ$ , and agrees in its physical and chemical properties with Harrow's carbopyrotritaric acid. When heated with soda-lime, it yields an oil (probably dimethylfurfurane) insoluble in water, and when heated with water at  $200^\circ$  a substance soluble in water. According to Harrow, carbopyrotritaric acid does not yield normal salts, but is converted, when boiled with an alkali, into the normal salt of an acid,  $\text{C}_8\text{H}_{10}\text{O}_6$ ; the author, however, obtains normal carbopyrotritarates in this way. When the acid is dissolved in ammonia and the excess of the latter is expelled by boiling, the hydrogen ammonium salt is obtained. The hydrogen silver salt,  $\text{C}_8\text{H}_7\text{AgO}_5$ , is stable, and the normal salt,  $\text{C}_8\text{H}_6\text{Ag}_2\text{O}_5$ , unstable when exposed to light.

It should seem that the acid obtained by Baeyer and Perkin (Abstr., 1884, 838) from ethyl dibenzoylsuccinate is also a furfurane-derivative, namely, diphenylfurfuranedicarboxylic acid.

By the action of aqueous or alcoholic ammonia on ethyl diacetosuccinate, *ethyl dimethylpyrrolinedicarboxylate*,  $\text{NH} \begin{matrix} \swarrow \\ \text{CMe} : \text{C.COOEt} \\ \searrow \\ \text{CMe} : \text{C.COOEt} \end{matrix}$ , is produced, isomeric with the compound obtained by the reduction of ethyl isonitroso- $\beta$ -imidobutyrate. Analogous pyrroline-derivatives are formed by the action of aniline, paratoluidine, and  $\beta$ -naphthylamine.

A. K. M.

**Derivatives of Ethyl Acetophenoneacetoacetate and of Ethyl Acetonylacetoacetate.** By C. PAAL (*Ber.*, 17, 2756—2767).—By the dehydration of acetophenoneacetone the author obtained two isomeric compounds of the formula  $\text{C}_{11}\text{H}_{10}\text{O}_3$  (Abstr., 1884, 1177). The one melting at  $82-83^\circ$  the author names *dehydracetophenoneacetone*, and ascribes to it one of three formulæ:  $\text{CPh} : \text{C.CH}_2.\text{COMe}$ ;  $\text{COPh.CH}_2.\text{C} : \text{CMe}$ ; or  $\text{COPh.CH}_2.\text{CH}_2.\text{C} : \text{CH}$ : the other, melting at  $41-42^\circ$ , he considers to be *phenylmethylfurfurane* (*phenylmethyltetratriphenol*), to have the formula  $\begin{matrix} \text{CH} : \text{CMe} \\ \text{CH} : \text{CPh} \end{matrix} > \text{O}$ , and to be formed according to the equations:—

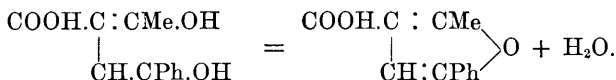


A better yield of phenylmethylfurfurane is obtained when fuming hydrochloric acid is substituted for acetic anhydride: when this is done no dehydracetophenone-acetone is formed.

Ethyl acetophenone-acetoacetate yields analogous dehydrated deriva-

tives. When poured into boiling alcoholic potash it yields an acid,  $C_{12}H_{10}O_3$ , already described. This compound, which shows the properties of an unsaturated ketonic acid, the author designates *dehydroacetophenone-acetonecarboxylic acid*, and believes to be the carboxylic acid of dehydracetophenone-acetone just described. This acid is not a stable compound, and when boiled with mineral acids is converted into a stable isomeric acid, which forms white glistening needles melting at  $180-181^\circ$ ; when the new acid is heated with water in sealed tubes at  $240-250^\circ$ , it splits up into phenylmethylfurfurane and carbonic anhydride, and is therefore undoubtedly *phenylmethylfurfuranecarboxylic acid*.

$COOH.C : CMe$   
acid,  $\begin{array}{c} | \\ CH : CPh \end{array} \rangle O$ . Its formation from the ketonic acid is probably to be explained by supposing an addition of water to the latter when treated with the mineral acid, and a simultaneous conversion of the ketonic groups into unsaturated alcoholic groups. The compound so formed would then again give up the elements of water and form an internal oxide:—



This acid begins to sublime at  $100^\circ$ , and yields long needles of the unchanged acid: it is easily soluble in alcohol, benzene, ether, &c. It is also decomposed into the furfurane by long-continued boiling with mineral acids, and very easily and completely by distillation over zinc-dust. It does not combine with phenylhydrazine. The alkali salts are easily soluble in water, the others less so.

Ethyl acetonylacetate, already prepared by Weltner (Abstr., 1884, 746), when treated with fuming hydrochloric acid yields ethyl pyrotritartarate. The acid obtained from this ether was proved to be identical with pyrotritartaric acid. From analogy with the above reactions the author believes pyrotritartaric acid to have the constitution

$COOH.C : CMe$   
 $\begin{array}{c} | \\ CH : CMe \end{array} \rangle O$ , and not to be a ketonic acid as hitherto believed.

This view is strengthened by the fact that this acid does not combine with phenylhydrazine. If this view is correct, carbopyrotritartaric acid must be looked upon as dimethylfurfuranedicarboxylic acid,  $\begin{array}{c} < C(COOH) : CMe \\ < C(COOH) : CMe \end{array} \rangle O$ . The author considers it very probable that all compounds containing the  $-CO.CH_2.CH_2.CO-$  group are readily convertible into furfurane-derivatives. Pyrotritartaric acid when heated with water at  $150-160^\circ$  undergoes a peculiar reaction, yielding a ketone,  $C_6H_{10}O_2$ , which boils at about  $187^\circ$ , is easily soluble in water, and combines readily with phenylhydrazine to form a crystalline compound. The author believes it to be acetonylacetone.

*Bromophenylmethylfurfurane tetrabromide*,  $C_{11}H_9Br_4O$ , is obtained by adding the furfurane to an excess of cold bromine: during the reaction, the temperature should be kept low enough to keep a part of the bromine frozen. This compound forms bronze-coloured, metallic-



looking scales, which are insoluble in the usual solvents in the cold, and decompose on heating. It blackens at  $200^{\circ}$  and melts at  $208-210^{\circ}$ . *Tetrahydrophenylmethylfurfurane* (*phenylmethyltetramethylene oxide*) is obtained by the reduction of an alcoholic solution of the furfurane with sodium. It forms a colourless mobile oil which distils without decomposition at  $230^{\circ}$ . It is insoluble in water and alkalis, but miscible in all proportions in alcohol, ether, &c. It does not react with phenylhydrazine, and can be boiled with sodium without decomposition: it therefore contains neither ketonic oxygen nor hydroxyl.

With hydroxylamine, dehydracetophenone-acetoacetic acid forms a compound,  $C_{12}H_{12}N_3O_3$ , which crystallises in white scales soluble in ether, alcohol, mineral acids, and alkalis, but only very sparingly in water. It turns brown at  $150^{\circ}$ , and melts with decomposition at  $172^{\circ}$ . This reaction is remarkable as, although the acid contains only one carbonyl-group, it enters into reaction with 2 mols. of hydroxylamine. With phenylhydrazine, this acid forms a very unstable compound,  $C_{18}H_{16}N_2O_2$ , which crystallises from water in small yellow needles.

When phenylmethylfurfuranecarboxylic acid is boiled with a large excess of acetic anhydride, a compound,  $C_{14}H_{12}O_4$ , is formed, which crystallises in flat plates soluble in alcohol, ether, and benzene: it melts at  $80-83^{\circ}$ . It is at once dissolved by aqueous caustic soda with re-formation of the original acid. The author is now investigating this compound.

Besides the compound,  $C_{17}H_{16}N_2$ , already described (*loc. cit.*), the author, by the action of phenylhydrazine on an ethereal solution of acetophenone-acetone, has obtained another compound,  $C_{17}H_{18}N_2O$ , which crystallises in well-formed prisms easily soluble in ether and benzene. It melts at about  $105^{\circ}$ , but is exceedingly unstable, even at ordinary temperatures.

When ethyl acetophenone-acetoacetate is boiled with dilute hydrochloric acid, it yields phenylmethylfurfuranecarboxylic acid together with a small quantity of phenylmethylfurfurane. The oil obtained by Weltner was probably a mixture of these two compounds.

L. T. T.

**The Thiophene Group.** By V. MEYER and O. STADLER (*Ber.*, **17**, 2778—2779).—The authors have endeavoured to obtain amido-derivatives of thiophene by the reduction of the nitro-derivatives, but although they have tried a great variety of reducing agents, they have up to the present been unsuccessful; entire decomposition has always set in. They find, however, that the thiophene-derivatives have much more intense colouring properties than the benzene-derivatives. When mononitrothiophene is boiled with alkalis, it dissolves to a brownish-red solution. Mononitrothiophenesulphonic acid is at once converted into a magenta-coloured solution by the action of ammonium sulphide. When dinitrothiophene, in alcoholic solution, is treated with a very small quantity of potash, it gives a very brilliant dark-red solution; this is due to the presence of a potash salt which the authors have obtained as a reddish-violet varnish, by precipitation with ether. Excess of alkali or acid destroys the colour. The magenta coloration (first observed by Hofmann) obtained when a drop of caustic potash is added to an alcoholic solution of commercial dinitrobenzene, is due

to the presence therein of dinitrothiophene; dinitrobenzene, prepared from benzene free from thiophene, does not show this reaction.

L. T. T.

**A Simple Method of obtaining Thiotolene and Thioxylene.**

By K. E. SCHULZE (*Ber.*, **17**, 2852—2854).—This method consists in submitting the acid used in the purification of xylene and toluene to distillation with steam. If the acid be first diluted with water, less sulphurous anhydride is evolved, whilst the yield of oil is greater: 90 per cent. of the oil distilled between 135—138°, and contained 44 per cent. thioxylene. The oil obtained from the acid used in purifying toluene yielded, on rectification, a product boiling at 111—112° and containing 22·3 per cent. thiotolene; a portion also boiled at about 80°, and from its reaction with isatin and sulphuric acid evidently contained thiophene.

The author intends to examine the acids used in the purification of benzene, naphthalene, and phenol.

A. K. M.

**The Benzene Theory.** By E. LELLMANN (*Ber.*, **17**, 2719—2723).—

The author describes comparative quantitative experiments on the readiness with which the hydrochlorides of ortho-, meta-, and paranitranilines are decomposed by water, the result being that the ortho-compound is the most readily acted on, the para-compound coming next, whilst metanitriline hydrochloride is least acted on. The introduction of a nitro-group into aniline is thus seen to diminish the basicity of the latter, least of all when it takes up the meta-position, and most of all when it occupies the ortho-position. The author also refers to many well-known observations that show the greater influence of the ortho- and para- over the meta-position on certain reactions, and that by the introduction of a nitro- or hydroxyl-group into a simple benzene-derivative, the chemical properties of the latter are affected to a less or greater extent, according as the group introduced is in the meta-, para-, or ortho-position. The diagonal formula of benzene appears to offer a better explanation of the above relation than either Kekulé's or the prismatic formula.

A. K. M.

**Monochlorethylbenzene.** By ISTRATI (*Bull. Soc. Chim.*, **42**, 111—116).—If a current of ethylene is passed into a mixture of phenyl and aluminium chlorides, there is formed a mixture of the three monochlorethylbenzenes,  $C_6H_5ClEt$ . On fractional distillation, the greater part passes over between 179—182°, and consisted of the ortho-, meta-, and para-derivatives in the proportion 7 : 10 : 3. The portion of the liquid boiling between 180—181° is an agreeably smelling liquid of sp. gr. 1·075; when exposed to a freezing mixture small crystals are deposited, probably the para-derivative. With sulphuric acid, this liquid forms three sulphonic acids, differing in appearance and solubility; it is proposed to make these the subject of a future memoir.

V. H. V.

**Monobromoparaxylene.** By P. JANNASCH (*Ber.*, **17**, 2709—2711).—A reply to Jacobsen (this vol., p. 144). The properties pre-

viously assigned by the author to this compound are confirmed (see *Annalen*, **171**, 79). A. K. M.

**Acetyltoiuene.** By J. C. ESSNER and E. GOSSIN (*Bull. Soc. Chim.*, **42**, 95—98).—Acetyl chloride and toluene, when heated with small quantities of aluminium chloride, form *acetyltoiuene*, an aromatic liquid boiling at 224—225°; sp. gr. at 22° = 0.9891. As this substance on oxidation with potassium permanganate yields metaphthalic acid, together with only the smallest traces of the ortho- and para-acids, it must have the constitution  $C_6H_4\overline{Ac}Me$  ( $\overline{Ac} : Me = 1 : 3$ ). On oxidation with nitric acid, it seems to form a toluic acid. V. H. V.

**Action of Phosphoric Chloride on Ethers of the Benzene Series.** By A. COLSON (*Compt. rend.*, **99**, 975—977, and *Bull. Soc. Chim.*, **42**, 152—156).—Paraxylene monethylin dissolves in dilute hydrochloric acid even below 100°, yielding dichloro-xylene, alcohol, and water. Other ethylins of the benzene series behave in the same way, but the reaction is slower. If the paraxylene monethylin is allowed to remain in contact with phosphoric chloride in the cold, the same product is formed, but if 10 grams of the ethylin are heated with 12—14 grams of the chloride until the latter just melts, an impure oily chlorethylin is formed, which after some months deposits terephthalic acid. When paraxylene monethylin is heated with two and a half times its weight of phosphoric chloride, hydrogen chloride, phosphorus trichloride, phosphoryl trichloride, and monochloroethane are given off, and the liquid in the flask acquires a wine-red colour. If this liquid is thrown into water, heat is developed, and as the solution cools colourless needles of terephthalic aldehyde are deposited, identical in their properties with the terephthalic aldehyde described by Grimaux, but the greater part of the product sinks to the bottom as a heavy liquid which soon crystallises. By continually treating this liquid with boiling water, the yield of terephthalic aldehyde is considerably increased. The fact that the compound thus obtained readily reduces tin salts and ammonio-silver nitrate, shows clearly that it is a true aldehyde, and not a phthalide.

Methylbenzyl oxide when heated with phosphoric chloride in the same way, yields benzaldehyde, and hence it would seem that the reaction is general amongst the ethers of the benzene series.

In all probability, the phosphoric chloride in the cold, or at about 100°, acts simply as a chlorinating agent, and forms dichloro-xylene, but at a higher temperature (about 175°) it dissociates into phosphorus trichloride and chlorine, and the latter attacks the methyl-groups in the dichloro-xylene, and converts them into methylene dichloride, thus producing the compound  $C_6H_4(CHCl_2)_2$ , which is decomposed by water with formation of terephthalic aldehyde and hydrochloric acid. It must be observed, however, that when the chlorethylin is heated with phosphoric chloride, it yields no terephthalic aldehyde, hence possibly the reaction is more complicated than that just indicated. In any case it is evident that when phosphoric chloride acts on the ethers of the benzene series, it attacks the lateral chains. C. H. B.

**Action of Benzoic Chloride on Isodurene in Presence of Aluminium Chloride.** By J. C. ESSNER and E. GOSSIN (*Bull. Soc. Chim.*, **42**, 170—174).—The action of benzoic chloride on durene has already been studied by Friedel, Crafts, and Ador (*Abstr.*, 1879, 713). The isodurene employed by the authors was obtained by the action of methyl chloride on toluene. The portion of the crude product boiling at 185—195° was cooled repeatedly to 20°, in order to separate the greater part of the durene, and the portion remaining liquid was then converted into sulphonic acids, and the sodium salts were treated with hydrochloric acid at about 210°. In this way, tolerably pure isodurene is obtained, the greater part of which boils at 185—190°.

Isodurene is mixed with half its weight of benzoic chloride, and aluminium chloride added. The reaction takes place readily in the cold, with development of heat, and when all evolution of hydrochloric acid ceases, benzene is added, and the product washed with water. On distillation, the crude product yields a yellow viscous liquid, boiling between 250° and 360°. After some days, this liquid deposits a mass of crystals, which are washed with alcohol to remove the adhering liquid, and purified by recrystallisation from boiling alcohol. The first alcoholic washings deposit a further quantity of the crystals by spontaneous evaporation.

These crystals are benzoylisodurene,  $C_6HMe_4.COPh$ ; they melt at 62—63°, and boil at about 300°. When treated with potassium hydroxide, they yield potassium benzoate and isodurene. Benzoylisodurene dissolves readily in sulphuric acid, forming a sulphonic acid, which is only slightly soluble in cold water, but very soluble in ether. When treated with nitrosulphuric acid, benzoylisodurene yields a yellow liquid nitro-derivative, and a product which dissolves in water, and seems to be a nitro-derivative of some acid formed in the reaction.

Benzoylisodurene in alcoholic solution combines with hydrocyanic acid, and when the product (which is difficult to purify) is boiled with alcoholic potash, ammonia is evolved, and if the solution is neutralised with hydrochloric acid, evaporated to dryness, and the residue extracted with absolute alcohol, an acid is obtained, which forms a white powder soluble in water, alcohol, and ether. The sodium salt crystallises in lamellæ. The silver salt on analysis gave numbers agreeing with the formula  $C_6HMe_4.CPh(OH).COOAg$ . The acid is therefore *phenylisodurylglycollic acid*. When benzoylisodurene is heated at 250° with fuming hydriodic acid, it yields benzylisodurene or benzyltetramethylbenzene,  $C_6HMe_4.CH_2Ph$ . Ador and Rillet have shown that the isodurene obtained by Friedel and Crafts' method is identical with Jannasch's  $\beta$ -durene, so that in benzylisodurene and benzoylisodurene the methyl-groups must be in the positions [2 : 3 : 4 : 6].

When an ethereal solution of benzoylisodurene is placed above an aqueous solution of hydrogen sodium carbonate, and treated with metallic sodium, it yields a yellow oil, which boils above 360°, and is either an alcohol or a pinacone, but its composition approaches most nearly to that of phenyl isoduryl carbinol. When this substance is heated with benzoic acid, and the crystalline product washed with water and then crystallised from ether, phenyl isoduryl carbinol ben-

zoate,  $C_6HMe_4.CPh.O\bar{B}z$ , is obtained in colourless crystals, which melt at  $75^\circ$ . The acetate is obtained by heating the crude product with acetic anhydride in sealed tubes at  $100^\circ$ . It is a yellowish oil, boiling above  $360^\circ$ .

When oxidised by a hot or cold solution of potassium permanganate, benzoylisodurene yields an acid, which appears to be benzoylbenzenetetracarboxylic acid,  $CPh.C_6H(COOH)_4$ . No pentacarboxylic acid is formed even when the permanganate is in very large excess.

Durene when treated with benzoyl chloride under the above conditions is only very slightly attacked, and a mixture of durene and isodurene yields benzoylisodurene and unaltered durene, without any mixed ketone.

C. H. B.

**Carbonates of Bivalent Alcohols and Phenols.** By M. WALLACH (*Annalen*, **226**, 77—87). — *Isohydrobenzoïn carbonate* is formed when ethyl chlorocarbonate acts on the sodium compound of isohydrobenzoïn. The bicarbonate could not be obtained. *Hydrobenzoïn carbonate* is prepared by an analogous reaction. The sodium compound required for its preparation, can only be obtained by the action of sodium amalgam on a solution of hydrobenzoïn in benzene. The carbonate crystallises in needles melting at  $126^\circ$ , which dissolve freely in alcohol and ether.

Ethyl ethylenebicarbonate,  $C_2H_4(O.COOEt)_2$ , is formed by the action of ethyl chlorocarbonate on the sodium compound of ethylene alcohol, but it has not been obtained in a state of purity. It is decomposed on distillation, apparently yielding ethylene carbonate and ethyl carbonate. The author has repeated Bender's (*Ber.*, **13**, 696) experiments on the action of ethyl chlorocarbonate on bivalent phenols, but has in some instances arrived at different results; namely, from resorcinol he obtained ethyl resorcinylbicarbonate,  $C_6H_4(O.COOEt)_2$ , a thick oil boiling between  $298^\circ$  and  $302^\circ$ , miscible with alcohol and ether. It is decomposed by prolonged boiling into monoethylresorcinol. Orcinol also yields an analogous compound,  $C_6H_3Me(O.COOEt)_2$ , which boils at  $311^\circ$ . It is decomposed by continuous boiling, yielding monethylorcinol.

W. C. W.

**Action of Phosphorus Trichloride on Aniline.** By C. L. JACKSON and A. E. MENKE (*Amer. Chem. J.*, **6**, 89, and *Chem. News*, **50**, 220). — In 1865 Tait described the product of the action of phosphorus trichloride on aniline as a white salve-like mass, of the composition  $(NHPh)_3P_3.HCl$ , easily soluble in water, alcohol, and ether, and yielding a platinochloride and several double salts. The authors have investigated this subject, and have cogent reasons for contesting the above statement.

The action of phosphorus trichloride on aniline is very energetic, when 3 molecular proportions of aniline are added to 1 mol. of trichloride. The product is a hard white solid, which is a mixture of substances, and obstinately resists all attempts at purification; a large number of solvents were tried, in all of which, with the exception of water, methyl and ethyl alcohol, and acetone, it is insoluble.

When, however, the trichloride is added to a large excess of aniline, Tait's salve-like mass is obtained. This contains, amongst other substances, aniline hydrochloride; and as Tait purified his substance by simply washing it with water, it is evident that the aniline hydrochloride would remain mixed with it. With excess of trichloride, the product is a white compact mass. Both the latter products are, to a considerable extent, soluble in ether; this the authors consider to be due to their respective solubilities in the excess of aniline in one case, and the excess of trichloride in the other. When the original product is heated in a dish over a naked flame, it turns orange-red, and aniline hydrochloride and a gas containing phosphorus volatilise, whilst the residue yields a colourless solution with alcohol, and an orange-coloured or red insoluble substance containing 81.73 per cent. of phosphorus. On the addition of water to the alcoholic solution, a white precipitate of  $(\text{NHPh})_2\text{PHO}$  is formed, aniline hydrochloride and phosphite remaining in solution. Attempts to obtain  $(\text{NHPh})_2\text{PCl}$  were made, but without success. *Phosphorus anilide*,  $(\text{NHPh})_2\text{PHO}$ , prepared as described above, forms, after purification, a white amorphous substance, readily soluble in cold alcohol and ether, insoluble in cold water; it melts at  $87^\circ$ , has no acid or basic properties, and is not affected by acids or alkalis in the cold. Alcoholic soda attacks it with difficulty; but boiling with strong hydrochloric acid for 12 hours decomposes it completely into aniline hydrochloride and phosphoric acid; whereas by gently heating it with nitric acid, a red solution is produced, from which water precipitates a red resinous body containing phosphorus, whilst a *nitrophenol* remains in solution; in one case trinitro-, in another metadinitro-phenol were obtained. By heating it with acetic anhydride and fused sodium acetate, *acetanilide* is formed. From these results, the authors conclude that the product of the action of phosphorus trichloride on aniline, which is soluble in water, consists of aniline hydrochloride and  $\text{NHPh.PCl}_2$ . When this mixture is heated, the two substances act on one another, producing  $(\text{NHPh})_2\text{PCl}$ , which in its turn is converted into the insoluble  $(\text{NHPh})_2\text{PHO}$  by the combined action of alcohol and water. If the original product is boiled for some time with excess of aniline, a mixture of substances is obtained, amongst which are crystalline substances melting at  $150^\circ$  and  $208^\circ$ , and apparently a substance with a higher melting point.

The substance melting at  $208^\circ$  forms small white prisms, apparently monoclinic, or long radiating needles. It is freely soluble in hot, less so in cold alcohol, insoluble in water and in ether. Aqueous potash or sulphuric acid does not act on it in the cold, but when boiled with either of them, it is gradually decomposed. Heated with hydrochloric acid at  $140^\circ$  under pressure, it yields phosphorous and phosphoric acids, aniline hydrochloride, some carbon, and gives an odour of phenol; its formula is possibly  $(\text{NHPh})_7\text{P}_3\text{O}_2\text{H}_2$ . The substance melting at  $150^\circ$  has been very imperfectly examined; it crystallises in rather thick white radiating needles.

D. A. L.

**Derivatives of Amidoethylbenzenes.** By H. PAUCKSCH (*Ber.*, 17, 2800—2806).—The ortho- and para-compounds are best separated

by means of the different solubilities of their acetyl-derivatives; acetylparamidoethylbenzene is sparingly soluble, the ortho-compound very easily soluble in water. The para-compound solidifies at  $-8^{\circ}$  to  $-10^{\circ}$ , and remelts at  $-5^{\circ}$ ; the ortho-compound does not solidify at these temperatures. Both bases resemble the corresponding toluidines in character.

*Benzoylorthamidoethylbenzene* is obtained by heating the base on the water-bath with benzoic chloride. It crystallises in small flakes melting at  $147^{\circ}$ . *Benzoylparamidoethylbenzene* forms long needles melting at  $151^{\circ}$ . When heated with phosphoric acid, orthophenylethylthiocarbamide is decomposed, yielding the phosphate of the base and orthophenylethylthiocarbimide. The latter is a colourless mobile liquid, which boils with partial decomposition at  $240-245^{\circ}$ . *Orthamidoethylbenzenesulphonic acid* is formed by the action of concentrated sulphuric acid on acetylorthamidoethylbenzene. It forms glistening white needles. With potassium nitrite and dimethylaniline, it forms a colouring matter crystallising in dark-orange scales. The analogous diethylated compound is amorphous.

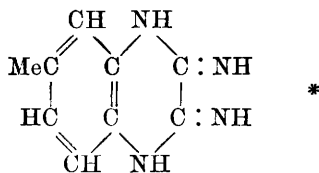
*Diparethylphenylcarbamide*,  $\text{CO}(\text{NH}.\text{C}_6\text{H}_4\text{Et})_2$ , is formed by the action of carbonyl chloride on paramidoethylbenzene. It crystallises in long needles, and melts at  $217^{\circ}$ . *Diparethylphenylguanidine*,  $\text{CNH}(\text{NH}.\text{C}_6\text{H}_4\text{Et})_2$ , is formed by heating diparethylphenylthiocarbamide, dissolved in alcoholic ammonia, with excess of lead oxide. It crystallises in large plates melting at  $137-138^{\circ}$ . It is easily soluble in alcohol, ether, and carbon bisulphide. It dissolves readily in concentrated hydrochloric acid, and yields a platinochloride which crystallises in scales.

When 1 molecular proportion of dichloroacetic acid is heated on the water-bath with 4 of paramidoethylbenzene in alcoholic solution, a mixture of two compounds is obtained. The one is a colourless compound, which is soluble in alcohol, insoluble in boiling water or hydrochloric acid, and sublimes at  $220-225^{\circ}$ . The other is undoubtedly parethylphenylparethylimesatin, analogous to the compound obtained by P. J. Meyer (Abstr., 1884, 47), although the author was unable to entirely free it from the other substance. When heated with hydrochloric acid, it dissolves, ethylisatin being formed, which crystallises in red needles melting at  $137^{\circ}$ . There is thus no doubt as to the identity of the imesatin.

L. T. T.

**Action of Cyanogen on Aromatic Diamines.** By J. A. BLADIN (*Bull. Soc. Chim.*, **42**, 104—111).—Cyanogen combines with aromatic diamines to produce compounds of the general formula  $\text{C}_n\text{H}_{2n-8}\text{N}_4$ , which form two series of salts, containing 1 and 2 mols. of a monobasic acid respectively. These substances, when heated with hydrochloric acid at the temperature of boiling water, give off one  $\text{NH}$ -group in the form of ammonia; at a higher temperature, two  $\text{NH}$ -groups are separated, thus: (1)  $\text{C}_n\text{H}_{2n-8}\text{N}_4 + \text{H}_2\text{O} = \text{C}_n\text{H}_{2n-9}\text{N}_3\text{O} + \text{NH}_3$  and (2)  $\text{C}_n\text{H}_{2n-8}\text{N}_4 + 2\text{H}_2\text{O} = \text{C}_n\text{H}_{2n-10}\text{N}_2\text{O}_2 + 2\text{NH}_3$ . In this paper, the derivatives of orthophenylene and metaparatoluenediamine are described.

*Dicyanometa-para-toluenediamine*,  $C_9H_{10}N_4$ , obtained by saturating a solution of meta-para-toluidine with cyanogen, forms colourless crystals containing 1 mol. of water. The following constitutional formula is assigned to it:—



Its hydrochlorides,  $C_9H_{10}N_4 \cdot 2HCl$  and  $C_9H_{10}N_4 \cdot HCl$ , crystallise in colourless needles; its platinochlorides,  $(C_9H_{10}N_4)_2 \cdot H_2PtCl_6 + 2H_2O$  and  $C_9H_{10}N_4 \cdot H_2PtCl_6 + 2H_2O$ , crystallise in small needles and tablets respectively; the sulphate,  $C_9H_{10}N_4 \cdot H_2SO_4 + H_2O$ , forms a white crystalline powder. On heating the base with hydrochloric acid at  $100^\circ$ , there is obtained a substance of formula  $C_9H_9N_3O$ , which crystallises in small needles, melts at  $290^\circ$ , and is sparingly soluble in water and alcohol; its hydrochloride, nitrate, and sulphate crystallise in needles; its platinochloride is amorphous.

When heated with hydrochloric acid at  $150^\circ$ , the base yields two substances of the composition  $C_9H_9N_3O$  and  $C_9H_8N_2O_2$ , of which the former is probably isomeric with the above-mentioned compound; the latter crystallises in silky needles, and is probably a dihydroxy-toluquinoxaline.

*Dicyano-ortho-phenylenediamine*, obtained by passing cyanogen into an alcoholic solution of orthophenylenediamine, forms pale yellow rhombic tables, sparingly soluble in water, and melts at  $280^\circ$ . Its constitutional formula is written thus:  $C_6H_4 \begin{smallmatrix} \text{NH.C(NH)} \\ \text{NH.C(NH)} \end{smallmatrix} >$ .

Its platinochlorides,  $(C_6H_8N_4)_2 \cdot H_2PtCl_6 + 3H_2O$  and  $(C_6H_8N_4) \cdot H_2PtCl_6 + H_2O$ , crystallise in yellow needles. When heated with hydrochloric acid at  $100^\circ$ , it yields a compound of the formula  $C_8H_7N_3O$ , crystallising in needles which melt at  $280^\circ$ ; but if the reaction be effected at  $150^\circ$ , there is formed a *dihydroxyquinoxaline*,  $C_8H_6N_2O_2$ ; this crystallises in long needles, melts at  $280^\circ$ , is sparingly soluble in water, and forms metallic salts.

V. H. V.

**Constitution of the Hydrazines.** By E. FISCHER (*Ber.*, 17, 2841—2846).—In this paper the author shows that the hydrazines have the constitution represented by the formulæ  $NHPh \cdot NH_2$  and  $NPhMe \cdot NH_2$ , and not  $NH_2Ph : NH$  and  $NHPhMe : NH$ , as assumed by Erlenmeyer (*Abstr.*, 1883, 1103).

A. K. M.

**Decomposition of Diazo-compounds by Alcohol.** By E. WROBLEWSKY (*Ber.*, 17, 2703—2704).—A question of priority.

**Action of Quinones on Amidophenols.** By T. ZINCKE and A. HEBEBRAND (*Annalen*, 226, 60—76).—By the action of benzoquinone

\* This formula, together with others, is incorrectly written in the original memoir.—V. H. V.



on orthamidophenol in hot alcoholic solution, quinol and a base of the composition  $C_{24}H_{18}N_4O_4$  are produced. The latter is deposited in needle-shaped crystals of a violet colour, but the former remains in solution. The crystals melt at  $250^\circ$ , and at a higher temperature yield a red crystalline sublimate. The compound is soluble in aniline, but is dissolved with difficulty by the usual solvents. It is decomposed by hot potash or soda lye with evolution of ammonia. It dissolves in dilute acids, forming salts which dissociate in the presence of a large quantity of water. The *hydrochloride*,  $C_{24}H_{18}N_4O_4 \cdot 2HCl$ , has a green metallic lustre. It dissolves freely in alcohol, and is sparingly soluble in water. It yields crystalline double salts with mercuric, stannic, zinc, and platinum chlorides. The *platinochloride* forms broad needle-shaped crystals of a brownish-red colour, which dissolve in hot water. The *sulphate* is a green crystalline powder; the *oxalate* forms green needles soluble in alcohol, and the *picrate* steel-blue needles melting at  $235^\circ$  with decomposition.

The *acetyl*-derivative,  $C_{24}H_{16}N_4O_4 \cdot \overline{Ac}_2$ , crystallises in brown needles or plates (melting at  $285^\circ$ ), and dissolves freely in benzene and in glacial acetic acid. The *benzoyl*-derivative,  $C_{24}H_{16}N_4O_4 \cdot \overline{Bz}_2$ , forms yellow needles which melt at  $264.5^\circ$ , and are soluble in hot acetic acid and in benzene.

Cautious oxidation with nitric acid converts the acetyl-derivative into oxalic acid and a nitro-product,  $C_{24}H_{15}(NO_2)N_2O_6$ , which is deposited from its solution in acetic acid in golden plates. The crystals begin to blacken at  $265^\circ$ , and melt between  $275^\circ$  and  $280^\circ$ . The nitro-compound dissolves in alkalis, forming a violet solution, from which alcohol precipitates a crystalline compound. Tin and hydrochloric acid reduce the nitro-product, forming a crystalline double salt. Aniline unites with it to form a crystalline compound of a dark blue colour, melting at  $229^\circ$ .

On the addition of sodium nitrite to a solution of the hydrochloride,  $C_{24}H_{18}N_4O_4 \cdot 2HCl$ , a red crystalline compound is deposited which has the composition  $C_{24}H_{16}N_4O_4(NO)_2$ .

II. Benzoquinone has no action on the acetic derivatives of orthamidophenol, but it enters into double decomposition with orthamidophenyl methyl ether, according to the equation  $3C_6H_4O_2 + 2OMe.C_6H_4.NH_2 = C_6H_3(NH_2.C_6H_3.OMe)_2O_2 + 2C_6H_4(OH)_2$ .

The substitution-product crystallises in reddish-violet needles which melt at  $230^\circ$ . It has neither acid nor basic properties.

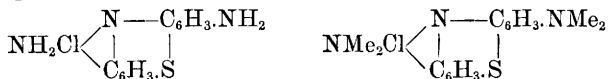
III. Benzoquinone acts on paramidophenol according to the equation  $3C_6H_4O_2 + 2NH_2.C_6H_4.OH = C_6H_3(NH_2.C_6H_3.OH)_2O_2 + 2C_6H_4(OH)_2$ . The best results are obtained when a hot aqueous solution of the hydrochloride is employed. The crystalline product dissolves freely in dilute alkalis, but is sparingly soluble in the usual solvents. It is a phenol, not a base.

IV. The products of the action of benzoquinone on the paramidocresols are phenols. The orthamido-derivative of orthocresol yields a red crystalline base, melting at  $284^\circ$ , insoluble in alcohol. The hydrochloride, platinochloride, and the acetic derivatives of the base are crystalline.

V. Amidothymol is oxidised to thymoquinone by benzoquinone.

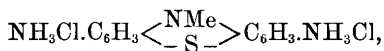
VI. No bases are formed by the action of benzoquinone on amido- $\beta$ -naphthol, or on its hydrochloride. W. C. W.

**Methylene-blue and Allied Dyes.** By A. BERNTHSEN (*Ber.*, 17, 2854—2862).—In a previous paper (*Abstr.*, 1884, 1156), reasons were given for concluding that Lauth's violet and methylene-blue have the following constitutions; in confirmation of these the author now brings further proof:—



By the introduction of two amido-groups into methylthiodiphenylamine,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{NMe} \\ | \\ \text{S} \end{array} \text{C}_6\text{H}_4$ , diamidomethylthiodiphenylamine,

$\text{NH}_2.\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{NMe} \\ | \\ \text{S} \end{array} \text{C}_6\text{H}_4.\text{NH}_2$ , is produced, but owing to the presence of the methyl-group this does not yield a dye corresponding with Lauth's violet. By the action of fuming nitric acid on methylthiodiphenylamine, a dinitrosulphoxide,  $\text{NMe}(\text{C}_6\text{H}_3.\text{NO}_2)_2\text{SO}$ , is obtained crystallising in small needles; it is insoluble in dilute alkalis. Diamidomethylthiodiphenylamine hydrochloride,



obtained on reducing the last compound, forms colourless prisms almost insoluble in hydrochloric acid, but readily soluble in water. By the action of ferric chloride on a solution in dilute hydrochloric acid, a very instable bluish-green compound is produced. Lauth's violet can be obtained, not only by introducing amido-groups into thiodiphenylamine, but also by heating paradiamidodiphenylamine with sulphur, and oxidising the product with ferric chloride,  $\text{NH}(\text{C}_6\text{H}_4.\text{NH}_2)_2 + 2\text{S} = \text{NH}(\text{C}_6\text{H}_3.\text{NH}_2)_2\text{S} + \text{SH}_2$ , and further from paranitraniline and sulphur.

If thiodiphenylamine be treated with weaker nitric acid than was previously employed (*loc. cit.*), a mononitro-derivative is produced, together with the dinitro-compound. This *mononitrodiphenylamine sulphoxide*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{NH} \\ | \\ \text{SO} \end{array} \text{C}_6\text{H}_3.\text{NO}_2$ , yields *amidothiodiphenylamine*,

$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{NH} \\ | \\ \text{S} \end{array} \text{C}_6\text{H}_3.\text{NH}_2$ , on reduction; the latter crystallises in white silky scales, somewhat soluble in hot water, readily in alcohol and ether; it oxidises readily, but is much more stable than Lauth's white; the hydrochloride,  $\text{C}_{12}\text{H}_8(\text{NH}_2)\text{NS}.\text{HCl}$ , forms small scales readily soluble in water, very sparingly in concentrated hydrochloric acid. Amidothiodiphenylamine is converted by ferric chloride into a

violet-red dye, the constitution of which,  $\text{HN} \begin{array}{c} \diagup \text{N} - \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_3.\text{S} \end{array}$ , should correspond with that of Lauth's violet. This *imidothiodiphenylimide* forms small, rusty-brown, spear-shaped crystals, moderately soluble in alcohol,

but less so in ether; the hydrochloride,  $C_{12}H_8N_2S.HCl$ , is very soluble in water and in alcohol; the zinc double salt,  $2C_{12}H_8N_2S.HCl + ZnCl_2$ , is readily soluble. The salts of imidothiodiphenylimide dye silk violet-red with a shade of brown. Amidothiodiphenylamine may also be obtained by heating paramidodiphenylamine with sulphur, hydrogen sulphide being abundantly evolved.

When hydroxydiphenylamine is melted with sulphur, *hydroxythiodiphenylamine*,  $C_6H_4 < \begin{smallmatrix} S \\ N \end{smallmatrix} > C_6H_3.OH$ , is produced. On extracting the product with dilute hydrochloric acid, dissolving the residue in aqueous alcohol and a little hydrochloric acid, and adding ferric chloride, a brown precipitate of *oxythiodiphenylimide*,  $C_{12}H_7NSO$ , is obtained. This substance dissolves very sparingly in the ordinary solvents, more readily in toluene and cumene, and very readily in aniline. It has neither basic nor acid properties. Hydroxythiodiphenylamine is re-formed on oxidising oxythiodiphenylimide. It has no basic properties, but its ready solubility in alkalis indicates its phenolic character.

A. K. M.

**Chrysaniline.** By O. FISCHER and G. KÖRNER (*Annalen*, **226**, 175—191).—Nearly all the contents of this paper have been previously published (Abstr., 1884, 748). *Chrysaniline*,  $C_9H_{15}N_3 + 2H_2O$ , crystallises in long golden-yellow needles, or in yellowish-brown, flat, spear-shaped crystals. When heated, it sinters together with loss of its water of crystallisation at about  $150^\circ$ , and melts at  $267$ — $270^\circ$ . It is sparingly soluble in alcohol. A solution of chrysaniline in hot benzene yields, after a time, golden-yellow plates of a compound of the formula  $C_{19}H_{15}N_3.C_6H_6$ .

A. J. G.

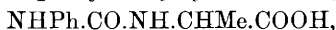
**Action of Phenyl Isocyanate on Amido-compounds.** By B. KÜHN (*Ber.*, **17**, 2880—2885).—Amides of monobasic acids react with phenyl isocyanate according to the general equation  $NPh : CO + RCO.NH_2 = NPhH.CO.NH.COR$ .

To prepare *phenylbenzoylcarbamide*,  $NHPh.CO.NHBz$ , dry benzamide is heated with phenyl isocyanate at  $150^\circ$ , until the odour of carbanil has disappeared. The product forms long silky needles, melting at  $199^\circ$ ; it dissolves readily in alcohol, sparingly in ether, and is insoluble in water. When it is heated, it breaks up into phenyl cyanate and benzamide. *Phenylpropionylcarbamide*,  $NHPh.CO.NH.C_3H_5O$ , prepared from propionamide and phenyl isocyanate, crystallises in concentrically grouped prisms, melts at  $137^\circ$ , dissolves sparingly in boiling water, readily in alcohol and ether, and is decomposed by heat into its constituents. *Phenylacetylcarbamide*,  $NHPh.CO.NHAc$ , melts at  $183^\circ$  (see also this Journal, 1876, i, 400). *Diphenylacetylcarbamide*,  $NHPh.CO.NPhAc$  (*loc. cit.*), may be obtained from acetanilide and phenyl isocyanate, whilst analogous compounds are also formed from formanilide, benzanilide, acetophthalide, and benzonaphthalide with phenyl isocyanate. The aromatic amido-acids also react with phenyl isocyanate, although less readily than the acid amides. *Phenyluramidobenzoic acid*,  $NHPh.CO.NH.C_6H_4.COOH$ , is prepared by heating together metamidobenzoic acid and phenyl isocyanate for 1—2 hours

at 100°; it is soluble in alkalis and in alcohol, sparingly also in ether, but is insoluble in water; it crystallises in concentrically grouped prisms, melting with decomposition at 270°, but does not yield a condensation-product like the corresponding uramidobenzoic acid.

The fatty amido-acids react somewhat differently with phenyl isocyanate. *a*-Amidopropionic acid yields diphenylcarbamide, and apparently also phenylmethylhydantoin:— $\text{NPhCO} + \text{NH}_2\text{CHMe.COOH} = \text{NPhH.CO.NH.CHMe.COOH}$ ;  $\text{NPhH.CO.NH.CHMe.COOH} + 2\text{NPhCO} = \text{CO} \begin{array}{c} \text{NPh.CO} \\ | \\ \text{NH-CHMe} \end{array} + \text{CO(NHPh)}_2 + \text{CO}_2$ . The phenyl-

methylhydantoin has not been isolated, but after boiling the product with alcoholic potash, *phenylmethylhydantoic acid*,



was obtained; this is insoluble in cold, readily soluble in hot water, also in alkalis, alcohol, and ether; it melts at 170° with decomposition.

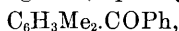
Phenyldiazine reacts with phenyl isocyanate with considerable development of heat. The product is *diphenylsemicarbazide*,



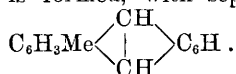
it crystallises from dilute alcohol in stellate-groups of needles, is sparingly soluble in hot water, readily in alcohol, and insoluble in ether; it melts at 170°. Naphthylhydrazines yield similar compounds.

A. K. M.

**Paraxylyl Phenyl Ketone.** By K. ELBS and E. LARSEN (*Ber.*, 17, 2847—2849).—By the action of aluminium chloride (50 grams) on a mixture of paraxylene (36 grams), benzoic chloride (47 grams), and carbon bisulphide (80—100 grams), paraxylyl phenyl ketone,



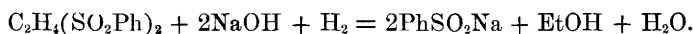
is obtained. It melts at 36°, boils at 303° (uncorr.), and distils extremely slowly in steam; it is insoluble in water, sparingly soluble in glacial acetic acid, but very readily in alcohol, ether, acetone, chloroform, light petroleum, and benzene, and crystallises from alcohol in large well-formed prisms. Its solution in glacial acetic acid is not attacked by chromic acid even on boiling. Paraxylyl phenyl ketone may be oxidised, however, by dissolving it in cold concentrated sulphuric acid, adding chromic mixture and boiling; the chief product of the oxidation is *benzoylparatoluic acid*. When the ketone is boiled for several days in a reflux apparatus, methylanthracene is formed, with separation of water:  $\text{C}_6\text{H}_3\text{Me}_2\text{COPh} - \text{H}_2\text{O} =$



A. K. M.

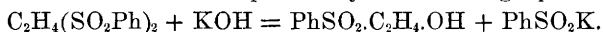
**Disulphones.** By R. OTTO and H. DAMKÖHLER (*J. pr. Chem.* [2], 30, 171—208).—*Ethylene diphenylsulphone*,  $\text{C}_2\text{H}_4(\text{SO}_2\text{Ph})_2$ , is obtained by a method similar to that employed by Otto in the preparation of the disulphoxides (Abstr., 1882, 831), namely, by heating a solution of sodium benzenesulphinate with ethylene dibromide and alcohol for

some time in a reflux apparatus. The unaltered ethylene dibromide and alcohol are distilled off; the disulphone separates from the residue on cooling, and is freed from sodium bromide and sodium benzenesulphinates by washing with water. By crystallisation from alcohol, ethylene diphenylsulphone is obtained in long, colourless, odourless needles; it is sparingly soluble in hot water, soluble in boiling alcohol and in benzene, very easily soluble in hot glacial acetic acid, and melts at  $179.5-180^{\circ}$ . Nascent hydrogen in presence of acids has no action on ethylene diphenylsulphone, whereas in alkaline solutions (by sodium amalgam and water), it is converted into sodium benzenesulphinates and ethyl alcohol, thus:—

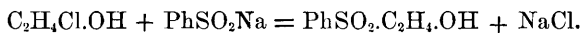


Chlorine acts on ethylene diphenylsulphone, producing sulphuryl chloride, benzenesulphonic chloride, ethylene dichloride, and chlorobenzenes; the action of chlorine in direct sunlight is somewhat different, the products being various chlorobenzenes and sulphuryl chlorides. Bromine does not attack the disulphone.

*Phenylsulphonethyl alcohol*,  $\text{PhSO}_2\text{CH}_2\text{CH}_2\text{OH}$ , is obtained by heating ethylene-diphenylsulphone with aqueous potash on a water-bath, and subsequent extraction of the liquid with ether. On evaporation, the ethereal solution leaves this compound as a colourless syrupy liquid, which has a neutral reaction and an intensely bitter taste; it is miscible with alcohol and benzene, and but sparingly soluble in water. Its formation is explained by the following equation:—

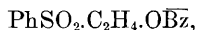


This alcohol has also been prepared synthetically by heating an aqueous solution of sodium benzenesulphinates with ethylene chlorhydrin in sealed tubes at  $120^{\circ}$ ; its formation is represented by the equation—



It is not acted on by nascent hydrogen in acid solutions, but nascent hydrogen in alkaline solutions converts it into ethyl alcohol and benzenesulphonic acid or thiophenol.

The following derivatives of this alcohol have been prepared by the ordinary methods:—The *acetate*,  $\text{PhSO}_2\text{C}_2\text{H}_4\text{OAc}$ , is a syrupy colourless liquid, having a bitter taste; it does not solidify at  $-12^{\circ}$ , and is miscible with alcohol, benzene, and ether. The *benzoate*,



forms white, shining, silky needles melting at  $124-125^{\circ}$ ; it is insoluble in water, but easily soluble in alcohol and chloroform, less easily soluble in ether.

*Phenylsulphonethyl hydrogen sulphate*,  $\text{PhSO}_2\text{C}_2\text{H}_4\text{SO}_4\text{H}$ , is formed by mixing the alcohol with sulphuric acid; on diluting with water, phenylsulphonethyl oxide separates out. The filtrate from this is neutralised with barium carbonate, and after removal of the barium sulphate yields, on spontaneous evaporation, barium phenylsulphonethyl sulphate,  $(\text{PhSO}_2\text{C}_2\text{H}_4\text{SO}_4)_2\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$ , which crystallises in needles having a vitreous lustre. The salt is soluble in water, its

aqueous solution is decomposed by boiling, with formation of barium sulphate, sulphuric acid, and the alcohol.

*Phenylsulphonethyl chloride*,  $\text{PhSO}_2\cdot\text{C}_2\text{H}_4\text{Cl}$ , is obtained by acting with phosphorus pentachloride on phenylsulphonethyl alcohol; also by acting with hydrochloric acid on the alcohol in sealed tubes at  $150^\circ$ . It crystallises from hot benzene in lustrous six-sided tablets, is soluble in benzene and alcohol, but sparingly soluble in water, and melts at  $55-56^\circ$ . In all its properties, this compound resembles the alkyl chlorides; when heated with sodium benzenesulphinate, it yields ethylene-diphenylsulphone, and when acted on with sodium paratoluenesulphinate, ethylene-phenylparatolylsulphone,



is obtained; this crystallises in small, white, lustrous needles melting at  $162^\circ$ .

Sodium-amalgam, in presence of alcohol, converts phenylsulphonethyl chloride into ethyl alcohol and sodium benzenesulphinate; zinc and hydrochloric acid do not act on it.

*Diphenylsulphonethyl oxide*,  $(\text{PhSO}_2\cdot\text{C}_2\text{H}_4)_2\text{O}$ , is obtained by acting with silver oxide on phenylsulphonethyl chloride: it is also produced by the action of dehydrating agents on phenylsulphonethyl alcohol.

It is almost insoluble in water, slightly soluble in ether, and easily soluble in benzene and alcohol, from which solutions it separates in small, white, lustrous needles, or by slower evaporation in yellowish hard prisms melting at  $69-70^\circ$ . This compound is also formed in small quantities by the action of potassium hydroxide, and also of baryta, on ethylene diphenylsulphone.

P. P. B.

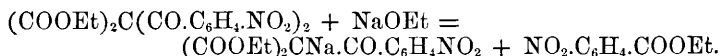
**Replacement of two Chlorine-atoms in Chlorides by Oxygen, by Means of Anhydrous Oxalic Acid.** By R. ANSCHÜTZ (*Annalen*, **226**, 13—22).—The anhydrides of mono- and bi-basic acids can be prepared by heating the acids with the theoretical quantity of anhydrous oxalic acid. The method yields excellent results.

The chlorides of aromatic aldehydes are converted into aldehydes by the action of anhydrous oxalic acid, for example, benzal chloride,  $\text{Ph}\cdot\text{CHCl}_2$ , yields benzaldehyde,  $\text{Ph}\cdot\text{CHO}$ , and chlorobenzal chloride,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHCl}_2$ , yields chlorobenzaldehyde,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ . Benzotrichloride,  $\text{Ph}\cdot\text{CCl}_3$ , under similar treatment, yields a mixture of benzoic anhydride and benzoic chloride, but if an excess of oxalic acid (3 mols. to 2) is used, the products consist of the pure anhydride.

W. C. W.

**Derivatives of Orthonitrobenzoic Acid.** By C. A. BISCHOFF and C. RACH (*Ber.*, **17**, 2788—2800).—Orthonitrobenzoic chloride was prepared from the nitro-acid by Claisen and Shadwell's method, and purified by crystallisation from ether. During this process, small quantities of a substance forming colourless needles were several times obtained. This substance proved to be *orthonitrobenzoic anhydride*. It is very sparingly soluble in water and ether, more soluble in alcohol, and melts at  $135^\circ$ . It is re-converted into the acid by alkalis. By the action of orthonitrobenzoic chloride on ethyl monosodomalonate, the authors obtained ethyl dinitrobenzoyl-malonate,  $(\text{COOEt})_2\text{C}(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ . This compound crystallises

in plates melting at 93°, and is the same substance previously described by Bischoff—who did not then obtain it pure—as ethyl nitrobenzoylmalonate (Abstr., 1883, 912). The yield of this compound was small, half the quantity of sodomalonate used being reconverted into ethyl malonate; small quantities of an oil were also formed, which exploded when heated above 170°. When treated with sodium ethylate, ethyl dinitrobenzoylmalonate yields ethyl sodonitrobenzoylmalonate and ethyl orthonitrobenzoate, according to the equation—



When an aqueous solution of this sodium-derivative is treated with hydrochloric acid, it yields *ethyl mononitrobenzoylmalonate*, which crystallises in colourless needles melting at 54°. Its alcoholic solution gives an intense bluish-red coloration with ferric chloride, and water then precipitates a bright red powder. Attempts to produce a substituted ethyl acetylenetetra-carboxylate from this ether were unsuccessful. When treated with bromine-vapour, the sodium compound just described yields *ethyl mononitrobenzoylbromomalonate*, which forms long prisms melting at 72°. When heated with excess of alcoholic ammonia in closed tubes at 100°, the dinitro-compound yields orthonitrobenzamide and ethyl malonate, together with a small quantity of malonamide. By the action of orthonitrobenzoic chloride on ethyl disodomalonate, the same dinitrobenzoyl-derivative is obtained as when the monosodo-compound is employed. If, however, equal molecular proportions of the chloride and of the ethyl disodomalonate are used, ethyl sodonitrobenzoylmalonate described above is formed. When ethyl disoacetylenetetra-carboxylate in alcoholic solution is treated with orthonitrobenzoic chloride, ethyl orthonitrobenzoate and ethyl acetylenetetra-carboxylate are formed. If the dry disodo-compound is suspended in ether and then treated with the chloride, ethyl dicarbontetra-carboxylate is formed, together with traces of a substance crystallising in needles melting at 150—158°, of ethyl acetylenetetra-carboxylate, and of a colourless oil volatile in a current of steam. When silver orthonitrobenzoate is added to acetic chloride, nitrobenzoic and acetic acids are formed.

L. T. T.

**Paramethoxyphenoxycinnamic Acid.** By A. VALENTINI (*Gazzetta*, 14, 147—150).—Oglialoro, by the action of benzaldehyde and acetic anhydride on sodium phenylglycollate, has obtained phenoxycinnamic acid together with cinnamic acid (Abstr., 1881, 276). In the present paper, the analogous reaction with anisaldehyde is studied, and it is shown that there are obtained *paramethoxy-cinnamic acid* and *paramethoxyphenoxycinnamic acid*; the former has been prepared synthetically by Perkin by heating anisaldehyde with sodium acetate and acetic anhydride (Trans., 1877, i, 408). The two acids may be separated from the crude crystalline product of the reaction by fractional crystallisation from aqueous alcohol, in which the paramethoxycinnamic acid is the less soluble. Paramethoxyphenoxycinnamic acid,  $\text{C}_6\text{H}_4(\text{OMe})\cdot\text{CH}:\text{C}(\text{OPh})\cdot\text{COOH}$ , crystallises in

yellowish-white rectangular tablets, which melt at  $200^{\circ}$ ; its methyl salt, obtained by saturating a warm mixture of the acid and methyl alcohol with hydrogen chloride, crystallises in white, rectangular laminæ melting at  $100^{\circ}$ . Thus the transformations of benzaldehyde and anisaldehyde are perfectly analogous.

V. H. V.

**Derivatives of Salicylic Acid.** By E. LIELMANN and R. GROTHMANN (*Ber.*, 17, 2724—2731).—*Bromonitrosalicylic acid*,  $C_6H_2Br(NO_2)(OH).COOH$  [ $COOH : OH : Br : NO_2 = 1 : 2 : 3 : 5$ ], may be obtained from nitramidosalicylic acid as follows: hydrobromic acid is added in four times the theoretical quantity to the nitramido-acid, the hydrobromide obtained dissolved in glacial acetic acid, nitrous anhydride passed through the solution, which is then warmed until no more nitrogen is given off, the product diluted with water and cautiously evaporated. It may also be obtained by the addition of bromine to a solution of nitrosalicylic acid in hot glacial acetic acid. Bromonitrosalicylic acid is readily soluble in hot, less so in cold water, very readily in alcohol and ether; it crystallises in needles or in nodules, and melts at  $222^{\circ}$ ; the *barium* salt,  $(C_7H_3BrNO_2)_2Ba + 4H_2O$ , and *calcium* salt,  $(C_7H_3BrNO_2)_2Ca + 6H_2O$ , are described. The *hydrochloride of bromamidosalicylic acid*, obtained by the action of tin and hydrochloric acid on bromonitrosalicylic acid, forms colourless needles readily soluble in water and alcohol, almost insoluble in ether; neither the free acid nor the platinochloride could be prepared. A diazo-derivative may be obtained crystallising in yellowish-brown lustrous scales and yielding  $OH.C_6H_3Br.COOH$  [ $COOH : OH : Br = 1 : 2 : 3$ ], on boiling with alcohol. This is sparingly soluble in cold, more readily in hot water and very readily in alcohol; it crystallises in needles melting at  $184^{\circ}$ , whilst the bromosalicylic acid obtained by Hübner and Heinzerling (*Zeit. f. Chem.*, 1871, 709) from bromamidobenzoic acid, [ $COOH : NH_2 : Br = 1 : 2 : 3$ ], melts at  $219-220^{\circ}$ . The authors confirm the constitution of their acid by heating it with water at  $180^{\circ}$ , by which means it yields carbonic anhydride and orthobromophenol. The *barium* and *calcium* salts,  $(C_7H_4BrO_3)_2Ba + 3H_2O$  and  $(C_7H_4BrO_3)_2Ca + 12H_2O$ , are described, and also the *lead* salt,  $C_7H_3BrO_3Pb$ . *Dibromosalicylic acid*,

$OH.C_6H_2Br_2.COOH$  [ $COOH : OH : Br = 1 : 2 : 3 : 5$ ],

may be obtained either by the action of hydrobromic acid on the above-mentioned diazo-derivative, or better by the addition of bromine to a cold dilute solution of salicylic acid in glacial acetic acid. It forms long colourless needles, melts at  $220^{\circ}$ , is almost insoluble in cold and only sparingly soluble in boiling water. The *barium* salt has the formula  $(C_7H_3Br_2O_3)_2Ba + 4H_2O$ ; the *lead* salt,  $C_7H_2Br_2O_3Pb$ , is insoluble. When the monobromosalicylic acid (m. p.  $165^{\circ}$ ) obtained by brominating salicylic acid (see Hübner and Heinzerling, *loc. cit.*) is nitrated, a bromonitrosalicylic acid, of the constitution

$OH.C_6H_2Br(ON_2).COOH$  [ $COOH : OH : NO_2 : Br = 1 : 2 : 3 : 5$ ]

is obtained. This melts at  $175^{\circ}$ , dissolves readily in hot, sparingly in cold water, and crystallises in clusters of short yellowish needles containing 1 mol.  $H_2O$ ; the following salts have been prepared:



$(C_7H_3BrNO_5)_2Ba$ ;  $(C_7H_3BrNO_5)_2Ca + xH_2O$ ;  $(C_7H_3BrNO_5)_2Pb$ ;  $C_7H_2BrNO_5Ba + 2H_2O$ ;  $C_7H_2BrNO_5Pb$ . *Dibromonitrophenol*,

$C_6H_2Br_2(NO_2).OH$   $[OH : Br : NO_2 : Br = 1 : 2 : 4 : 6]$ ,

is obtained as a secondary product in the preparation of the first described bromonitrosalicylic acid. It is sparingly soluble in water, more readily in alcohol, and crystallises in slender needles melting at  $142^\circ$ ; the barium derivative,  $(C_6H_2Br_2NO_3)_2Ba + 10H_2O$ , forms green needles. *Dibromamidophenol*,  $C_6H_2Br_2(NH_2).OH$ , obtained by the reduction of the nitro-compound, forms reddish-coloured needles melting at  $190^\circ$ ; it is sparingly soluble in cold, more readily in hot water, and still more so in alcohol. It does not yield salts.

A. K. M.

**Ethyleneamidobenzoic Acids.** By H. SCHIFF and C. PARENTI (*Annalen*, 226, 243—248).—*Ethylenedibenzamic acid*,

$C_2H_4(NH.C_6H_4.COOH)_2$ ,

is prepared by boiling ethylene bromide with a saturated alcoholic solution of metamidobenzoic acid for one day in a reflux apparatus. It forms a crystalline powder, melts at  $222$ — $225^\circ$ , is very sparingly soluble in water, readily soluble in boiling alcohol or in cold alkalis, and is also soluble in moderately concentrated hydrochloric acid. A neutral solution of the ammonium salt gives with cupric acetate a greenish-blue pulverulent precipitate of the cupric salt,  $C_{16}H_{14}N_2O_4Cu + H_2O$ , and with nickel chloride a pale green precipitate of the nickel salt. *Diethyl ethylenediethyldibenzamate*,  $C_2H_4(NEt.C_6H_4.COOEt)_2$ , prepared by heating ethylenedibenzamic acid with ethyl iodide and alcoholic potash, crystallises in colourless needles or prisms, melts at  $98$ — $100^\circ$ , and is insoluble in water.

In the preparation of ethylenedibenzamic acid there is formed at the same time another acid distinguished by its more sparing solubility in all solvents. It forms a yellow powder, does not melt when heated at  $300^\circ$ , and is probably a more condensed ethyleneamidobenzoic acid.

By the action of ethylene bromide on amidobenzamide at least two amides of ethyleneamidobenzoic acid are formed; beyond a statement as to their ready but unequal solubility in alcohol and in glacial acetic acid, no account is given of their properties.

A. J. G.

**Diethylphthalide.** By P. DE BERCHEM (*Bull. Soc. Chim.*, 42, 168—169).—100 grams of phthalyl chloride are heated at  $100^\circ$  with 450 grams of toluene, and 40 grams of aluminium chloride is added gradually. When the theoretical amount of hydrogen chloride has been given off, the reaction is stopped and the product thrown into water. The toluene containing the phthalide in solution is separated from the water, the toluene distilled off, the residue dissolved in alcohol, and purified by filtration through animal charcoal. Diethylphthalide,  $C_6H_4 \langle \overset{C(C_6H_4Me)_2}{\text{---CO---}} \rangle O$ , thus obtained forms prisms

which seem to be monoclinic, with an angle of  $63.15^\circ$ . These crystals melt at  $116^\circ$ , and are soluble in alcohol, ether, benzene, and toluene, but insoluble in water or aqueous potash. The yield is only 4—5 per cent., but six isomerides can exist, and possibly only one of them is a crystallisable compound.

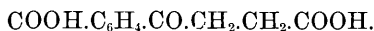
C. H. B.

**Diphthalyl.** By C. GRAEBE and P. GUYE (*Ber.*, **17**, 2851—2852).—When a mixture of phthalic anhydride and phthalide is boiled for 6—7 hours, water is set free and diphthalyl produced:  $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{O}$  +  $\text{C}_6\text{H}_4\langle\text{CH}_2\rangle\text{O} = \text{CO}\langle\text{C}_6\text{H}_4\rangle\text{C}:\text{C}\langle\text{C}_6\text{H}_4\rangle\text{CO} + \text{H}_2\text{O}$ . The product is extracted with alcohol or chloroform, when nearly pure diphthalyl remains behind. The reaction takes place more readily with thiophthalic acid in the place of phthalic anhydride.

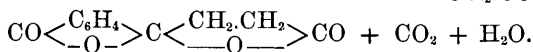
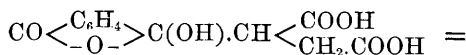
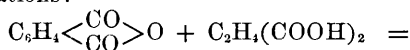
A. K. M.

**Phthalyl-derivatives.** Parts II and III. By W. ROSER (*Ber.*, **17**, 2770—2775 and 2775—2778).—When preparing ethinediphthalyl according to Gabriel's instructions, by heating together phthalic anhydride, succinic acid, and sodium acetate, the author succeeded in isolating two other compounds. When the melt is digested with boiling water, a *double lactone*,  $\text{C}_{11}\text{H}_8\text{O}_4$ , is extracted, and crystallises out on cooling. The residue is then boiled with alcohol, to get rid of a brown bye-product, and the pale yellow residue dissolved in boiling nitrobenzene. On cooling this solution, the yellow needles of ethinediphthalyl crystallise out first, but after a little time are accompanied by red needles of an isomeric compound, which the author names *isoethinediphthalyl*. This compound may be purified by crystallisation from aniline. Aniline dissolves both the yellow and red compound, but deposits the red needles again on cooling, whereas the yellow compound combines with the aniline and remains in solution.

The *double lactone*,  $\text{CO}\langle\text{C}_6\text{H}_4\rangle\text{C}\langle\text{CH}_2\text{CH}_2\rangle\text{CO}$ , crystallises in needles. It melts at  $120^\circ$  and is decomposed at  $240^\circ$ . It has no acid properties. When boiled with water, carbonates, or alkalis, it is converted into  $\beta$ -benzoylpropionorthocarboxylic acid,



This acid crystallises in hexagonal prisms, which melt at  $137^\circ$ , and are very soluble in water. When heated on the water-bath for some time, this acid is reconverted into the double lactone. The lactone dissolves in ammonia to a violet solution, which on the addition of acids deposits a compound crystallising in needles and containing nitrogen; this is probably phthalimidylacetic acid. The metallic salts of the carboxylic acid are insoluble or sparingly soluble in water. The author explains the formation of the lactone by the following equations:—



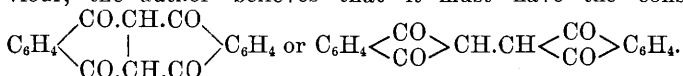
On reduction with sodium amalgam in the cold, the dibasic acid yields *phthalido- $\beta$ -propionic acid*,  $\text{C}_{11}\text{H}_{10}\text{O}_4$ , which crystallises in micaceous scales melting at  $121^\circ$ . It is easily soluble in boiling water,

alcohol, and ether. The metallic salts are easily soluble in water. When this acid is boiled with excess of barium hydroxide, the solution allowed to cool, the excess of barium removed by carbonic acid, and the solution evaporated in a vacuum over sulphuric acid, the *barium*, and from that the *silver* salt of the bibasic acid,



may be obtained. These salts are very unstable, and if the evaporation of the barium salt is carried out on the water-bath the phthalidic acid is reformed. This behaviour very closely resembles that of the alkali salts of diaterebic and diaterebilenic acids. Further reduction of the above acid yields phthalidobutyric-orthocarboxylic acid.

*Isoethinediphthalyl* is insoluble in water and alcohol, easily soluble in boiling nitrobenzene or aniline. It does not melt at  $280^\circ$ , and has the properties of a feeble acid. When boiled with alkalis, it forms violet solutions which deposit violet salts, but these salts are decomposed even by water. Neither acetic chloride nor anhydride nor phenylhydrazine have any action on this compound. From its behaviour, the author believes that it must have the constitution



PART III.—When phthalic anhydride, pyrotartaric acid, and sodium acetate are heated together at  $240\text{--}250^\circ$ , *propinediphthalyl*,  $\text{C}_{18}\text{H}_{12}\text{O}_4$ , is formed. This compound is soluble in alcohol and nitrobenzene, crystallises in yellow needles, is still solid at  $280^\circ$ , and is analogous in properties to ethinediphthalyl. If, however, during the reaction the temperature is allowed to rise to  $290^\circ$ , a considerable quantity of phthalylisopropylidene,  $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{C}:\text{C}(\text{Me})_2$ , already described by Gabriel, is formed. The author believes this compound to be produced by the decomposition of a double lactone analogous in constitution to that described above. When boiled with alkalis, it yields *benzoylisopropylorthocarboxylic acid*,  $\text{COOH.C}_6\text{H}_4.\text{CO.CHMe}_2$ . By the reduction of this acid with sodium amalgam, phthalidoisopropyl,  $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CH.CHMe}_2$ , is formed, which is easily volatile in steam.

L. T. T.

**Decomposition of Sulphonic Acids.** By C. FRIEDEL and J. M. CRAFTS (*Bull. Soc. Chim.*, **42**, 66—69, and *Amer. Chem. J.*, **6**, 182).—The authors, without questioning the priority of Armstrong and Miller's method for the regeneration of an aromatic hydrocarbon by the decomposition of its sulphonic acid (*Trans.*, 1884, 148), show that they have applied it to the separation of naphthalene tetrahydride from naphthalene. The sulphonic acid of the latter is the more readily decomposed, and when the mixed acids are mixed with sulphuric acid, heated to  $160^\circ$ , and a current of steam passed in, the greater part of the naphthalene distils over. The formation of oxidation products is thus completely avoided. The authors have applied this reaction to benzenesulphonic acid and its homologues, but have not, as they hoped, been able to extend it to the purification of

pentamethylbenzene, owing to difficulties in the preparation of the sulphonic acid. V. H. V.

**Preparation of Dinitrophenolsulphonic Acid.** By BEYER and KEGEL (*Dingl. polyt. J.*, **254**, 356).—On boiling potassium mononitrophenolparasulphonate, obtained from potassium phenolparasulphonate, with dilute nitric acid until all evolution of gas ceases, a yellow colouring matter is produced:  $\text{OH.C}_6\text{H}_3(\text{NO}_2).\text{SO}_3\text{K} + \text{HNO}_3 = \text{OH.C}_6\text{H}_2(\text{NO}_2)_2.\text{SO}_3\text{K} + \text{H}_2\text{O}$ . The same dye is obtained on boiling potassium phenolparasulphonate with an excess of dilute nitric acid thus:  $\text{OH.C}_6\text{H}_4.\text{SO}_3\text{K} + 2\text{HNO}_3 = \text{OH.C}_6\text{H}_2(\text{NO}_2)_2.\text{SO}_3\text{K} + 2\text{H}_2\text{O}$ . By treating phenolorthosulphonic acid or potassium mononitrophenol-orthosulphonate in a similar manner, an isomeric colouring matter is obtained, which gives the same shade when dyed, but dissolves more readily in water. This dye is produced also by heating potassium phenoldisulphonate with moderately dilute nitric acid. Diazobenzeneparasulphonic acid being converted into phenolparasulphonic acid when boiled with water, yields the same dye as phenolparasulphonic acid, whilst diazobenzenedisulphonic acid gives the same dye as phenoldisulphonic acid. D. B.

**Action of Aluminium Chloride.** By R. ANSCHÜTZ and H. IMMENDORFF (*Ber.*, **17**, 2816—2817).—It has been shown that aluminium chloride reacts with benzene and acetylene tetrabromide, with production of anthracene. The authors have repeated this reaction with toluene, the three xylenes, and with ethylbenzene in the place of benzene. Toluene, acetylene tetrabromide, and aluminium chloride yield a dimethylantracene, but it is obtained in much smaller quantity than anthracene is from benzene; the xylenes also yield methylated anthracenes, but in extremely small quantity, whilst no homologue of anthracene could be obtained from ethylbenzene. In all these reactions homologues of benzene are also produced, the formation of which appears to be independent of the acetylene tetrabromide. By the action of aluminium chloride on toluene, benzene and xylenes are obtained; metaxylene when similarly treated yields benzene, toluene, mesitylene, and pseudocumene, whilst ethylbenzene yields benzene and diethylbenzene. Dimethylantracene is also formed in small quantity by the action of aluminium chloride on boiling toluene.

A. K. M.

**The Hydrocarbon  $\text{C}_{16}\text{H}_{12}$  from Styrolene Alcohol.** By T. ZINCKE and A. BREUER (*Annalen*, **226**, 23—60).—The preparation of the hydrocarbon  $\text{C}_{16}\text{H}_{12}$  from styrolene alcohol, and the preparation of the quinhydrone and quinol derived from it, have been already described (*Abstr.*, 1878, 885, 889; 1879, 327; 1880, 665; and 1882, 207).

Aqueous sulphurous acid, stannous chloride, or hydriodic acid reduce the quinone to a quinhydrone and a quinol. The latter crystallises in colourless needles or plates which melt at  $92^\circ$ . In presence of moisture, it rapidly oxidises. The acetate,  $\text{C}_{16}\text{H}_{10}\text{OAc}$ , forms needle-shaped crystals melting at  $152^\circ$ .

The calcium and barium salts of the quinol,  $(\text{C}_{16}\text{H}_9\text{O}_3)_2\text{Ba}$ , form dark-coloured needles soluble in alcohol. The silver salt is a brown amorphous body insoluble in alcohol.

On oxidation with potassium permanganate, both the hydrocarbon and the quinone are converted into benzoic acid. The quinol under similar treatment yields benzoic and phthalic acids, but if the oxidation is conducted in an alkaline solution, an acid of the composition  $C_9H_6O_5$  is obtained instead of phthalic acid.

The constitution of the hydrocarbon may be represented by the formula  $PhC_4H_2Ph$ ; the constitutions of the quinone and the quinol have not yet been definitely ascertained. W. C. W.

**Japanese Camphor Oil.** By H. OISHI (*Chem. News*, **50**, 275—277).—When the woody parts of the *Laurus camphora*, growing on the southern coasts of the islands of Shikoku and Kiushiu, are distilled with water, the distillate contains solid camphor and an oil. The quantities obtained vary with the season; more of the former and less of the latter are obtained in winter than in summer, and *vice versa*. The crude oil when redistilled yields from 20 to 26 per cent. of camphor. The rectified oil is a colourless liquid, and burns with smoky flame; its sp. gr. at  $15^\circ$  is 0.895 (crude oil, sp. gr. = 0.959); rotatory power by Soleil saccharimeter =  $68.96^\circ$ . Treated with hydrogen chloride, it separates into two layers, the upper one transparent, the lower turbid. Nitric acid in the cold produces a similar effect, the upper layer being yellow, the lower colourless. When heated, the oil becomes red and oxidises, producing camphor and other oxidised products. Sulphuric acid dehydrates it, leaving a liquid with an odour resembling that of terpene; large quantities of this acid char the oil. Chlorine is absorbed by the oil with elevation of temperature and evolution of hydrogen chloride, the liquid becoming yellow and viscid. Bromine behaves in a similar manner, producing an amorphous red substance. Heated with iodine, which dissolves readily in it, the oil becomes red, and on cooling below  $0^\circ$  semi-solid. These reactions, coupled with analytical and physical data, lead the author to conclude that the oil is a mixture of terpenes, camphors, and some other oxidised hydrocarbons. The oil dissolves many resins, asphalt, sulphur, &c., and has been successfully applied as a solvent for varnishes. D. A. L.

**Bromonitro-camphor.** By P. CAZENEUVE (*Bull. Soc. Chim.*, **42**, 69—70).—The author has shown that dextrorotatory monochloro-camphor,  $C_{10}H_{15}ClO$ , yields a lævorotatory mononitro-derivative,  $C_{10}H_{14}(NO_2)ClO$ ; he now ascertains whether a similar, though inverse phenomenon, occurs on nitrification of monobromo-camphor. The substance,  $C_{10}H_{14}(NO_2)BrO$ , prepared according to the method indicated by Schiff (*Abstr.*, 1882, 526), crystallises in large prisms melting at  $103^\circ$ . For a 1 per cent. solution (temperature not given) the author found  $[\alpha]_D = -27^\circ$ ; the nitrobromo- and nitrochloro-camphor (so-called  $\alpha$ -derivative) thus belong to the same series. V. H. V.

**The so-called Oxycamphor of Kachler and Spitzer.** By H. GOLDSCHMIDT (*Ber.*, **17**, 2717—2718).—In reply to the above-named chemists, as to the identity of the "oxycamphor" with campholenic acid (this vol., p. 173), the author points out a difference of  $10^\circ$  in the boiling points and the strongly acid character of the latter substance.

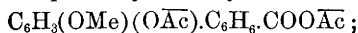
The existence of camphoroxime (*Ber.*, **16**, 494) is against Kachler and Spitzer's formula, whilst the formation of an amide by the action of heat on the ammonium salt, indicates the presence of a carboxyl-group in campholenic acid.

A. K. M.

**Convallaria Majalis (Lily of the Valley).** By A. LANGLEBERT (*Jour. Pharm.* [5], **10**, 26—30).—Two glucosides, convallamarin and convallarin, occur in *Convallaria majalis*. The author prepares *convallamarin* by extracting the whole plant with water, *convallarin*, not being soluble, is thus left behind. The extract is precipitated with lead acetate, and from this, by the action of a solution of tannin, a tannate of convallamarin is formed. The tannate dissolved in alcohol is precipitated by milk of lime, and the filtrate when evaporated gives the convallamarin as an amorphous powder. This substance is soluble in water, concentrated sulphuric acid, alcohol, ordinary, and methylic ether, chloroform, and amyl alcohol. Dissolved in monohydrated sulphuric acid, its colour is yellow, then reddish-brown, becoming violet on contact with water and moist air. The above method of treatment applied to an alcoholic extract of the whole plant gave a residue of convallarin, which differs from convallamarin only in its insolubility in water. Under the influence of dilute acids, convallamarin is resolved into glucose and convallamaretin, whilst convallarin gives glucose and convallaretin.

J. T.

**Substances obtained from Turmeric.** By C. L. JACKSON and A. E. MENKE (*Amer. Chem. J.*, **66**, 77—89) (compare *Abstr.*, 1881, 611; 1882, 1107; 1883, 480).—*Monacetocurcumin*,  $C_{14}H_{13}\overline{Ac}O_4$ , is a viscous brown mass; the acetyl-group replaces hydrogen in the phenolic hydroxyl. *Diacetocurcumin*,  $C_{14}H_{12}\overline{Ac}_2O_4$ , forms bright yellow crystals, melting at  $154^\circ$ ; it is probably an anhydride of the formula



with alkalis a red colour is produced only slowly.

Curcumin treated with phosphoric oxychloride yields a reddish-purple product, difficult of examination. Its reactions and analyses would show it to be an acid anhydride.

The action of hot potassium permanganate solution in excess on turmerol has been already studied (*Abstr.*, 1883, 482); terephthalic acid is formed. Using cold solutions, the whole of the oil was oxidised in about three days, some acetic and carbonic acids being formed; the filtered solution was acidified and extracted with ether, and the product distilled with steam. The distillate contains an acid, *turmeric acid*, forming a crystalline calcium salt,  $Ca(C_{11}H_{13}O_2) + 3H_2O$ , which is used for the isolation of the acid; water dissolves 1.27 per cent. of the salt at  $16^\circ$ . Free turmeric acid,  $C_{11}H_{14}O_2$ , is liberated by the action of hydrochloric acid on the calcium salt, it forms oily drops which slowly crystallise. It melts at  $34$ — $35^\circ$ , has a faint odour like that of cocoa-nut, is sparingly soluble in water, freely in other ordinary solvents. The silver, barium, and zinc salts were examined.

From the non-volatile residue, containing tarry products, a white crystalline acid separated; it was recrystallised from water. *Apoturmeric acid*,  $C_{10}H_{12}O_4$ , melts at  $221^\circ$ , and is easily soluble in hot water;

it forms the salts  $\text{CaC}_{10}\text{H}_8\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{BaC}_{10}\text{H}_8\text{O}_4 \cdot 2\text{H}_2\text{O}$  (?). The products of its oxidation could not be determined, but terephthalic acid is not formed.  
H. B.

**Catalpic Acid.** By SARDO (*Gazzetta*, **14**, 134—139).—Decoctions of the siliquaceous capsule of the *Bignonia catalpa*, a member of the Bignonia family, naturalised in Italy from America, are given in cases of asthma. By a prolonged extraction of these decoctions with ether, there is obtained an acid substance, together with a resin, which may be separated by frequent treatment with alcohol. The acid substance thus purified forms large, white crystals, melting at  $206^\circ$ , and resembling resorcinol in appearance; also very slightly soluble in water, but imparts to it a decided acid reaction; it is also soluble in alcohol and ether. Its barium salt forms white, glistening laminæ, its silver salt is a white precipitate, which rapidly turns brown, owing to some reducing action. The analyses of the acid and its barium and silver salts point to the formula  $\text{C}_{14}\text{H}_{14}\text{O}_6$ ; it is proposed to call the substance catalpic acid. It may be isomeric with hydrocardenic and akin to ipecuanic acid, which differs from it by 1 mol. of water and 1 of hydrogen, although both acids are bibasic.  
V. H. V.

**Decomposition of Pyridine Methiodides and Ethiodides by the Action of Alkalis.** By O. DE CONINCK (*Bull. Soc. Chim.*, **42**, 177—180).—When the methiodides and ethiodides of the pyridines derived from brucine and cinchonine are distilled with a slight excess of potassium hydroxide, in presence of a small quantity of water, decomposition takes place in three stages. In the first the products are neutral compounds with tinctorial properties; in the second, the products are pyridic, hydrides, whilst at a high temperature inflammable gases are given off.

In order to obtain the colouring matters, the methiodide or ethiodide, washed with ether and dried at a low temperature, is mixed with potash in lumps, water is added until the mixture becomes fluid, and the liquid is distilled on a sand-bath over a Bunsen flame. The distillate is exhausted with ether, the ethereal solution evaporated, and the residue taken up with methyl or ethyl alcohol. The colour of the products is intensified in a very marked manner by the addition of acids, especially acetic acid, whilst soda and potash change the colour to a dirty red. Ammonia, as a rule, produces no effect. Sometimes the addition of acids intensifies or produces fluorescence or modifies its character. These colouring matters are perfectly neutral. Those derived from brucine and cinchonine (in acetic acid solutions) dye silk various shades from straw colour to orange and light brown. Those derived from the bases from coal-tar produce the same shades, but, as a rule, have less tinctorial power.

Products of this kind were obtained from  $\alpha$ -picoline,  $\beta$ -lutidine,  $\gamma$ -lutidine,  $\alpha$ -collidine, and  $\beta$ -collidine. They give ethereal and alcoholic solutions of various shades of orange and red, with usually a well-marked fluorescence, both the colour and the fluorescence being frequently altered on addition of acetic acid. No analyses of these compounds are given. When the ethereal solutions are allowed to

evaporate spontaneously with exposure to air, a black resinous solid substance is deposited, which gradually becomes less soluble in alcohol and ether. Probably the oxygen liberated during the distillation with potash plays the same part as the oxygen of the air.

C. H. B.

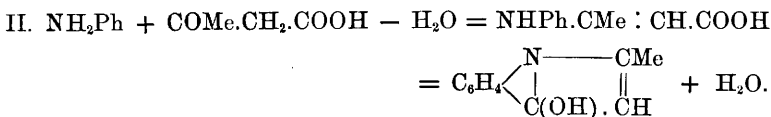
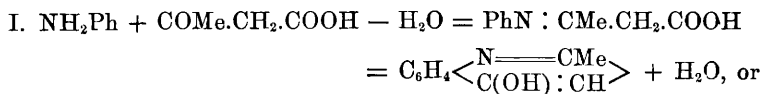
**Constitution of Pyridine-derivatives from Brucine.** By O. DE CONINCK (*Bull. Soc. Chim.*, **42**, 100—104).—In order to determine the constitution of the two lutidines present in the crude quino-line from brucine, the author has submitted them to oxidation by potassium permanganate, added cupric acetate to the product, and separated the copper salts formed, by fractional crystallisation. From the fraction melting between 155—170°, there were obtained nicotic and pyridine-monocarboxylic acids, together with formic and acetic acids. The oxidation of the  $\beta$ -lutidine contained in the original substance can be represented by the following equation:— $C_5H_4EtN + O_5 = C_5H_4N.COOH + H.COOH + H_2O$ . From the fraction melting between 185—200°, there were obtained on oxidation a methyl-pyridinecarboxylic acid and pyridinedicarboxylic or cinchomeric acid, the former of which melts at 211°. The oxidation of the collidine contained in the mixture can thus be represented as taking place in two successive stages; at the first, the ethyl- and then the methyl-group is oxidised thus:—(1.)  $C_5H_3NMeEt + O_5 = C_5H_3NMe.COOH + HCOOH + H_2O$ , and (2.)  $C_5H_3NMe.COOH + O_3 = H_2O + C_5H_3N(COOH)_2$ . It is proposed to carry on further researches regarding the constitution of these acids.

V. H. V.

**Constitution of Quinoline.** By L. KNORR and O. ANTRICK (*Ber.*, **17**, 2870—2880).—This research was undertaken in the hopes of being able to decide between the older formula assigned to

quinoline and that more recently suggested, namely,  $C_6H_4 \begin{matrix} \text{CH.CH} \\ | \quad || \\ \text{N} - \text{CH} \end{matrix}$ .

Knorr's synthesis of quinoline from aniline and ethyl acetoacetate (*Abstr.*, 1884, 1198) can be explained by either formula, thus:—



It is shown that at least the first stage of the synthesis takes place as in equation II, for when anilacetoacetic acid is dissolved in chloroform, and bromine added, two atoms of the latter are taken up, and on warming the solution, hydrobromic acid is evolved with formation of *monobromanilacetoacetic acid* ( $\alpha$ -bromophenyl- $\beta$ -amidocrotonic acid),  $NHPh.CMe : CBr.COOH$ , which is converted by sulphuric acid



into *bromoxyquinaldine*, I,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{N} \text{---} \text{CMe} \\ | \quad \parallel \\ \text{C}(\text{OH}) \cdot \text{CBr} \end{array}$ , or II,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{NH} \cdot \text{CMe} \\ | \quad \parallel \\ \text{CO} \cdot \text{CBr} \end{array}$ ;

this crystallises in silky needles melting at about  $258^\circ$ , is insoluble in water, soluble in alkalis and in acids, sparingly also in alcohol, ether, and chloroform. From its behaviour with nitrous acid, acetic anhydride, acetic chloride at  $130^\circ$ , methyl iodide at  $180^\circ$ , boiling phenylhydrazine, and hydroxylamine in alkaline and acid solutions,  $\gamma$ -oxyquinaldine appears to contain neither an imido- nor a carbonyl-group, and therefore to have the constitution indicated by formula I; its resemblance to carbostyryl, solubility in alkalis, its quantitative conversion (by fusion with phosphorus pentachloride) into monochloroquinaldine, and the production of quinaldine by distilling it with zinc-dust, likewise indicate the presence of a hydroxyl-group. When, however,  $\gamma$ -oxyquinoline is boiled with an excess of methyl iodide and an equivalent of sodium methylate in methyl alcohol, 1' : 2' *dimethyl-*

*pseudoquinoxyl*,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{NMe} \cdot \text{CMe} \\ | \quad \parallel \\ \text{CO} \text{---} \text{CH} \end{array}$ , is obtained; this compound may

also be prepared by heating ethyl acetoacetate with aniline at  $150^\circ$ , and digesting the product with concentrated sulphuric acid; the solution is then poured upon ice and supersaturated with alkali. It crystallises in slender needles melting at  $132^\circ$ , is readily soluble in alcohol, chloroform, and in acids, soluble in ether and water, but insoluble in alkalis; the platinochloride,  $(\text{C}_{11}\text{H}_{11}\text{NO})_2 \cdot \text{H}_2\text{PtCl}_6$ , forms slender needles melting at  $215^\circ$ . Dimethylpseudoquinoxyl remains unaltered when heated with 20 per cent. hydrochloric acid at  $180\text{--}200^\circ$ ; with bromine-water, it yields a bromine-derivative crystallising in white needles. It bears a strong resemblance to Hantzsch's methylpseudolutidostyryl (Abstr., 1884, 1045), and to Lieben and Haitinger's methylhydroxypyridine (Abstr., 1884, 1196).

2' : 3' *Methylchloroquinoline*,  $\text{C}_{10}\text{H}_8\text{NCl}$ , prepared by heating  $\gamma$ -oxyquinaldine with phosphorus pentachloride and a little oxychloride at  $135\text{--}140^\circ$ , crystallises in slender needles, is almost insoluble in water, readily soluble in alcohol, chloroform, and ether, melts at  $59^\circ$  and boils at about  $290^\circ$ . It dissolves readily in acids, and yields a platinochloride crystallising in cubes. Its chlorine may be displaced by boiling chloroquinaldine with alcoholic potash.

From the above, it is concluded that  $\gamma$ -oxyquinaldine is most probably 2' methylquinoxyl,  $[\text{N} : \text{Me} : \text{O} = 1' : 2' : 4']$ , but further experiments are being made with the view of deciding the question.

A. K. M.

**Dimethylquinoline II.** By L. BEREND (*Ber.*, 17, 2716--2717). A *dimethylquinoline* may be obtained from ordinary metaxylinidine  $[1 : 3 : 4]$ , in the same way as from orthoxylinidine (Abstr., 1884, 1197). It is a colourless, refracting, oily liquid, boiling at  $268\text{--}269^\circ$  (corr.); its sp. gr. at  $4^\circ$  is 1.0665. The *platinochloride*,  $(\text{C}_{11}\text{H}_{11}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$ , forms yellow needles sparingly soluble in hot water, the *acid sulphate*,  $\text{C}_{11}\text{H}_{11}\text{N} \cdot \text{H}_2\text{SO}_4$ , is a white crystalline powder; the dichromate crystallises from hot water in long needles. A sulphonic acid,  $\text{C}_{11}\text{H}_{10}\text{N} \cdot \text{SO}_3\text{H}$ , is obtained by the action of fuming sulphuric acid on the base at

160—170°; it is very readily soluble in water and hot alcohol, and crystallises in pale-yellow microscopic needles melting at 165—166°.

The above described dimethylquinoline is perhaps identical with the base obtained by Leeds by distilling acralxyldine (Abstr., 1883, 669).

A. K. M.

**Diquinoline from Benzidine.** By W. ROSER (*Ber.*, 17, 2767—2769).—The author gives the following proofs of the non-identity of the diquinoline obtained by him from benzidine (Abstr., 1884, 1371) with the  $\alpha$ -diquinoline of Weidel (Abstr., 1882, 69). The measurement of the crystals of the two compounds show decided differences; the axial ratio, for instance, is 1.33 : 1 : 1.05 in the author's compound, but 1.37 : 1 : 1.32 in Weidel's. Roser's compound gives additive compounds with 1 and with 2 mols. of methyl or ethyl iodide; Weidel's  $\alpha$ -diquinoline gives a mono-additive product, but no di-additive product could be obtained even when a large excess of iodide was employed.

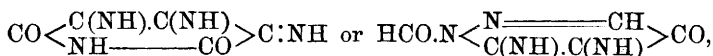
L. T. T.

**New Method for the Synthesis of Nitrogenous Organic Compounds: Synthesis of Xanthine and Methyl-xanthine.** By A. GAUTIER (*Bull. Soc. Chim.*, 42, 141—146).—A mixture of hydrocyanic acid and water is heated in sealed tubes with a quantity of acetic acid sufficient to keep the liquid acid. The products have a maroon or reddish-brown colour, and can be separated by taking advantage of the difference in their solubilities. One part of the contents of the tube is soluble in cold water, and consists of aldehydic acids which the author is investigating, and a yellow substance soluble in alcohol and oxidising in presence of air to a deep slaty-blue compound. If the alcoholic solution, made in the cold, is mixed with excess of hydrochloric acid and allowed to remain exposed to the air, it deposits purple microscopic crystals with the lustre of cantharides. It appears to be a weak bibasic acid, and yields a potassium salt, the colour of which is wine-red or rose, according to the proportion of alkali.

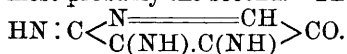
That portion of the crude product which is insoluble in cold water is exhausted repeatedly with boiling dilute acetic acid, and the precipitate which separates from the solution on cooling, is washed, redissolved in hydrochloric acid, neutralised with ammonia, filtered, mixed with copper acetate, and heated to boiling. Copper xanthate and methyl xanthate are precipitated, and are then decomposed by hydrogen sulphide, the resulting magma boiled with dilute hydrochloric acid, filtered, the filtrate neutralised with ammonia and concentrated until the xanthine and methyl-xanthine crystallise out on cooling. The two substances can be partially separated by fractional crystallisation. The xanthine thus obtained gives all the reactions of ordinary xanthine, and forms salts which are identical with ordinary xanthine compounds. The synthesis of xanthine and methyl-xanthine may be represented by the equation  $11\text{HCN} + 4\text{H}_2\text{O} = \text{C}_5\text{H}_4\text{N}_4\text{O}_2 + \text{C}_6\text{H}_5\text{N}_4\text{O}_2 + 3\text{NH}_3$ , but this does not take into account the compounds described above, or the azulmin which is formed in large quantity. If the water is replaced by various alcohols, ketones, phenols, aldehydes, &c., and the hydrocyanic acid by carbylamines, an almost

infinite series of complex bases, acids, and indifferent bodies can be obtained.

This synthesis of xanthine, together with results published in 1872 and 1873, and recent investigations, not yet published, respecting the relation between xanthine and the alkaloids derived from animal tissues, indicate that xanthine has one of the following constitutions :—



most probably the second. The constitution of sarcine will then be—



C. H. B.

**Synthesis of Homoquinine.** By O. HESSE (*Annalen*, **226**, 240—242).—The author has shown (Abstr., 1884, 1385) that homoquinine, when treated with potash, yields quinine, and fancied that it was the only product. Paul and Cownley, however, on repeating the experiment, found that besides quinine, another alkaloid, cupreine, is formed in about equal amount; the author now confirms their statement. *Cupreine* crystallises from ether in concentrically grouped small prisms, melts at 191°, dissolves without fluorescence in dilute sulphuric acid (the solution gives a green colour with chlorine and ammonia, less intense than that given by quinine), and yields compounds with both acids and bases. The normal sulphate forms slender prisms sparingly soluble in water; the hydrochloride crystallises in small needles, the sodium salt forms satiny plates. Homoquinine can be prepared artificially by dissolving equal molecular proportions of quinine and cupreine in excess of dilute sulphuric acid, precipitating with ammonia, and extracting the precipitate with ether; homoquinine then crystallises from the ethereal solution. A. J. G.

**Brucine.** By W. A. SHENSTONE (*Ber.*, **17**, 2740).—A question of priority.

**Brucine.** By A. HANSEN (*Ber.*, **17**, 2849—2850).—After obtaining nothing but oxalic acid by the action of potassium permanganate on brucine, the author tried boiling the latter with dilute chromic mixture. The product is poured into hot baryta-water, carbonic anhydride passed through the filtrate, which is then concentrated, the barium precipitated as sulphate, filtered, and the filtrate evaporated to a syrup; on cooling a vitreous mass is obtained which is insoluble in absolute alcohol, chloroform, and benzene. The product is an acid,  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_4$ , the platinochloride of which crystallises in magnificent golden-yellow scales containing 5 mols.  $\text{H}_2\text{O}$ .

By the action of phosphorus pentachloride on brucine, the author has also obtained a substance which yields a crystalline platinochloride. He intends to continue the experiments. A. K. M.

**Crystalline Metahæmoglobin from the Dog.** By G. HÜFNER (*Zeits. Physiol. Chem.*, **8**, 366).—Crystalline metahæmoglobin is as

readily prepared from oxyhæmoglobin from the dog, as from that from the pig. It closely resembles that from the latter source in all particulars.

A. J. G.

**Oxyhæmoglobin of the Horse.** By G. HÜFNER and M. BÜCHELER (*Zeits. Physiol. Chem.*, **8**, 358—365).—The substance was prepared in the usual manner from the separated corpuscles. The crystals obtained were usually large needles 2—3 mm. long and about 0.5 mm. thick; on one occasion, however, well formed hexagonal tables were observed. It contained about 3.94 per cent. of water. 100 c.c. of water dissolved 2.614 grams at 1° and 14.375 grams at 20°. Elementary analysis gave—

C.	H.	N.	S.	Fe.	O.
54.40	7.2	17.61	0.65	0.47	19.67

These numbers agree closely with those previously obtained by Kossel (*ibid.*, **2**, 150) and Otto (*Pflüger's Archiv*, **31**, 240). The mean of the results of the three observers would correspond with the approximate formula,  $C_{550}H_{852}N_{149}S_2FeO_{149}$ . On the assumption that 1 mol. of hæmoglobin combines with 1 mol. of carbonic oxide, 1 gram of oxyhæmoglobin should absorb 1.41 c.c. (at 0° and 1 mm. pressure) of that gas. It was found that the amount of oxygen displaced by treatment with carbonic oxide was 1.31 c.c. (mean of five determinations), and that the carbonic oxide compound on treatment with nitrogen gave up 1.39 c.c. of gas (mean of 14 determinations) per gram of oxyhæmoglobin.

A. J. G.

**New Forms of Albumose.** By W. KÜHNE and R. CHITTENDEN (*Amer. Chem. J.*, **6**, 101—120. Continued from Abstr., 1884, 1389; see also 849).—The methods of purification of *heteroalbumose* are described; it is well characterised by the appearances accompanying its coagulation. When dissolved in dilute (0.1—0.2 per cent.) hydrochloric acid the coagulum is in great part reconverted into *heteroalbumose*; a portion of *dysalbumose* is also formed. *Heteroalbumose*, unlike *prot-* and *dys-*albumose, is not precipitated by mercuric chloride; when acetic acid is added to the mixture, a heavy precipitate is formed.

Its mean composition is—

C.	H.	N.	S.	O.
50.74	6.72	17.14	1.16	24.24

Its specific rotary power was  $[\alpha]_D = -68.65^\circ$ .

*Dysalbumose* prepared from Witte's "pepton" gave on analysis—

C.	H.	N.	S.	O.
50.88	6.89	17.08	1.23	23.92

The specific rotary power could not be determined. The authors regard *dysalbumose* as a form of *heteroalbumose* which has become insoluble in neutral salt solution. *Protalbumose* and *dysalbumose* were found in the precipitate formed by addition of alcohol to the urine from a case of osteomalacia.

The authors consider that they have succeeded (1) in proving the existence of a series of bodies intermediate between albumins and peptones, the composition of which points to a gradual course of hydrolytic decomposition, and that these forms of albumose are to be considered collectively as the first hydrates; (2) in obtaining proof that the different forms of albumose not only fall apart into the anti- and hemi-group, but that now the hemi-group by itself can be considered as consisting of several members (namely, proto-, deuto-, hetero-, and dys-albumose). "Insoluble" hemialbumose consists of heteroalbumose, and "soluble" hemialbumose corresponds with both protalbumose and deutoalbumose, or with a mixture of both these bodies.

H. B.

**Basic Products (Ptomaines) from Human Corpses.** By L. BRIEGER (*Ber.* 17, 2741—2742).—The internal organs of corpses which had been left for 24—48 hours in a cool cellar, were cut up, treated with water and enough dilute hydrochloric acid to give a faintly acid reaction, the whole heated nearly to boiling, filtered hot, and evaporated. The syrup obtained was repeatedly treated with alcohol, platinic chloride added to the alcoholic solution, the precipitate dried and extracted with water, when choline platinochloride was obtained. The amount of choline obtained from the organs of one corpse is very small, and no other basic substance appears to be formed during the first stages of the decomposition. By further putrefaction more poisonous substances are formed; in one experiment a substance was obtained which resembles muscarine in its action on rabbits and Guinea pigs, and in the composition of its platinochloride.

A. K. M.

**Genesis of Ptomaines.** By F. COPPOLA (*Gazzetta*, 14, 124—130).—The author's recent researches on the genesis of ptomaines as products of cadaveric putrefaction, have tended to show on the one hand, that the arterial blood contains no such alkaloids, and on the other, that the processes, such as Dragendorff's, used for their extraction, are in themselves sufficient to produce them (*Abstr.*, 1883, 522, 624). These results have been confirmed by the experiments of Marino, who was able to extract traces only of neurine and lecithine from various physiological products, and of Mosso and Guareschi, who state that in the extraction of alkaloids by sulphuric acid (Dragendorff's process), the substances owe their formation for the most part to the decomposing action of the acid. Finally Mattei has demonstrated that death produced by the injection of aqueous extracts of fresh organs, is not due to a poisoning material within the organ, but to a purely infective process (*Abstr.*, 1884, 199). As these views are in opposition to those of Selmi, Schwanert, and others, the author has made experiments with blood, as a liquid which preserves its alkalinity in the process of its putrescent decomposition, and thus can be extracted by various solvents, without resource to the use of free alkali for the purposes of neutralisation. Blood taken from the carotid of a dog, and not defibrinated, was kept for two days at 30° and afterwards allowed to putrefy at the ordinary temperature without direct contact with air. The residue was then extracted with chloroform and benzene, and the extract tested with the ordinary reagents for the alkaloids, but the results were

negative, even after putrefaction had lasted for two months. The author calls particular attention to this fact, although he would not conclude therefrom that putrefaction is in no case sufficient of itself to cause the formation of the alkaloids.

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V. H. V.

## Physiological Chemistry.

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**Effects of Alkalis and Acids on Respiration.** By C. LEHMANN (*Landw. Versuchs-Stat.*, **31**, 169—171).—According to the author, the ashes of various cattle-foods have not been sufficiently studied from the point of view of their effect on the transformation of tissue in the respiratory organs. The general opinion is that the increase of alkalis in the circulation, causes increase of oxidation and consequent rapidity of tissue changes, whereas the preponderance of acids has a contrary effect. Experiments in this direction being very rare, the author undertook some researches with the view of deciding the question; the work of others is also noticed. The author's experiments were made on rabbits on which the operation of tracheotomy was performed after a fast of 18—24 hours; they were then placed in the respiration apparatus described in *Pflüger's Archiv*, 1884.

During spontaneous breathing of the animals after introduction of alkali into the stomach by the pump, there was an increase of oxygen consumption of more than 5 per cent., while after the introduction of acids there was a decrease of 8·3 per cent., the substances used being sodium carbonate and hydrochloric acid.

In order to obtain a more rapid action, the substances in a suitably dilute state were introduced directly into the veins (2 per cent. of  $\text{Na}_2\text{CO}_3$ —0·5 per cent.  $\text{HCl}$ ), and in order better to observe the muscular contractions, the animals were curarised and artificial respiration employed; after 1—2 hours from the time of the injection of the alkali, the consumption of oxygen had increased 4—5 per cent. and the production of carbonic anhydride to 7—20 per cent.; the injection of the dilute acid on the contrary, reduced the consumption of oxygen about 5 per cent., and also that of the carbonic anhydride considerably. In another series of experiments, using the same alkali and acid, but adding 3 per cent. of grape-sugar to each, it was shown that the non-nitrogenous matters were rendered more readily oxidisable by alkalis and less so by acids; in one case the alkali caused an increase of oxygen consumed of 15 per cent. and of carbonic anhydride produced of about 24 per cent. In order to show that the injection of the solutions into the veins was not the cause of abnormal irritation, the author injected solutions of common salt into other animals under precisely similar conditions, but the functions of the organism continued to be carried on normally.

J. F.

**Digestive Ferments.** By P. VIGIER (*Jour. Pharm.* [5], **9**, 398—402, 461—468; and **10**, 17—21).—1. *Pepsin*.—After many experi-

ments, the author proposes the following method for the estimation of pepsin:—Medicinal pepsin powder 0·5 gram; water 60; hydrochloric acid, officinal, 0·6; mutton, pork, or veal fibrin, washed and strained, 10 grams. Heat at 50° on water-bath for six hours, with frequent agitation until the fibrin is dissolved; this takes place very rapidly, then shake every hour; after six hours, 10 c.c. of the filtered liquor should give no turbidity on the successive addition of 30–40 drops of nitric acid; 0·2 gram of the pepsin extractive ought to give the same results. The aptitude of a pepsin to dissolve fibrin is a character of no value, for a good pepsin can dissolve three or four thousand times its weight of fibrin, if the amount of acidified water present is proportional to the amount of fibrin; the true test is the power to convert the fibrin into peptone. The author asserts that the only character which indicates in a precise manner that the digestion is complete, is the absence of all precipitation and turbidity on the addition of nitric acid. The fibrin employed should be obtained by vigorously stirring up warm blood with a bundle of twigs, washing in a large quantity of water until colourless, and then pressing in cloth. It may be preserved in glycerol, but the results are not so good as with fresh material. Results obtained by the author point to the fact that the accumulation of peptone in the solution tends to prevent further action of the pepsin, and that the action of the pepsin is considerably increased if the peptone produced be sufficiently diluted; hence the necessity of drinking sufficient fluid during a meal. These results appear to show that pepsin acts as a living ferment.

J. T.

**Behaviour of Carbonic Anhydride, Oxygen, and Ozone in the Human Stomach.** By W. JAWORSKI (*Zeits. f. Biol.*, 20, 234–254).—Whilst making experiments upon the behaviour of chloride of sodium solution in the human stomach, the author noticed that if the solution was saturated with carbonic anhydride it passed through much more rapidly than if no free carbonic anhydride were present. He accordingly made the following experiments, the results of which are briefly as follows:—

All the gases increase the quantity of secretion, although in varying proportions, a fact which proves that it is not from mechanical stimulation, but from the action of the gases themselves.

Carbonic anhydride very markedly increased the activity in two cases, but only a little in a third case; the acid secretion peptonised albumin readily, and had moreover a strongly antiseptic action.

Oxygen caused in one case the secretion of an alkaline fluid, which dissolved, but did not peptonise.

Ozone produced in one case a less alkaline secretion than oxygen, in another case very little change; the largest increase in the secretion is, however, produced by ozone.

Carbonic anhydride, besides producing a pleasant effect, stimulated the appetite.

J. P. L.

**Formation of Fat from Carbohydrates in the Animal Organism.** By S. CHANIEWSKI (*Zeits. f. Biol.*, 20, 179–192).—



Soxhlet's experiments on pigs and Schulze's on geese being inconclusive, the author made the present ones, in the hope of arriving at a more definite conclusion. For this purpose, three geese of nearly similar live weight were fed for 26 days on rice and barley, at the end of which period No. 1, weighing 3219 grams, was killed and used as the standard of comparison. No. 2 and No. 3 were then fed on a daily ration of 100 grams of a mixture of rice and barley, their respective weights before the commencement of the feeding, being No. 2, 3283 grams, No. 3, 3581 grams. After 18 days, No. 2 was killed, and weighed at that time 3816 grams. No. 3 was not killed till the 29th day; its weight had then increased to 4471 grams.

The total amount of proteïd and fat was determined in the dried flesh, bones, blood, feathers, &c., of each bird, and are compared in a table given in the original paper.

During the period of feeding, the intake and output of nitrogen balanced one another within the limits of experiment. The increase in proteïd in both birds was but a small percentage of the total.

Making every allowance for the fat assimilated from the food and that which was possibly due to the decomposed proteïd of the same, it is only necessary to subtract 75·37 grains for No. 2 and 136·52 for No. 3; a balance of 193·63 grams for No. 2 and 503·68 grams for No. 3 is still left, the origin of which apparently can only be from the carbohydrates.

A similar experiment made with two geese almost destitute of fat gave even a more striking result, 86·7 per cent. of the newly formed fat apparently being due to the carbohydrates. J. P. L.

**Alimentary Value of Oats.** By A. MUNTZ and C. GIRARD (*Ann. Agronomiques*, 10, 524—526; from *Ann. de l'Institut Agronomique*, No. 8).—Three horses were fed each with three varieties of oats from Sweden, Russia, and the Beauce district respectively. The rations were weighed and analysed before ingestion, and the excreta of the animals were also weighed and analysed, in order to determine the coefficient of digestibility of each constituent in the three samples of oats examined. Taking the coefficient of digestibility of the starch (none of which was excreted) as 100, the authors arrive at the following conclusions:—

*Nitrogenous Substances.*—80 per cent. (mean) of the nitrogen contained in the Beauce sample, 77·3 of that in the Russian sample, and 75 per cent. of that in the Swedish sample, was digested.

*Succharifiable Cellulose.*—56 per cent. of that in the Beauce oats, and about 34 per cent. of that in the other samples, was digested.

*"Indigestible fibre"* (the residue after successive treatment with acid and alkali).—45·2 per cent. of this was digested in the Beauce sample, 37·5 in the Swedish sample, and 18·5 only in the Russian sample.

The nutritive value of a sample of oats is greater the smaller the proportion of husk to kernel; in the cases cited, the Beauce oats contained much less husk than the Swedish.

The authors point out the erroneous results arrived at in estimating the nutritive value of a food such as oats, from an ordinary analysis.

They also mention that different samples of oats which they have examined, vary in the percentage of albuminoids from 7·6 to 13·25.

J. M. H. M.

**Digestibility of Substances used as Food for Horses.** By A. MUNTZ and C. GIRARD (*Ann. Agronomiques*, 10, 526—527; from *Ann. de l'Institut Agronomique*, No. 8).—Experiments made in the manner above described have yielded the following results:—

*Horse-beans.*—Horse No. 1 digested 67·64 per cent. of the nitrogenous matter, horse No. 3, 77·9 per cent.; crude fibre 46 (No. 1) and 81 (No. 3) per cent.; saccharifiable cellulose 73·6 (No. 1) and 88·3 (No. 3) per cent.

*Buckwheat.*—Supposing the grains to be perfectly masticated, which is never the case, the digestive coefficients are as follows:—fat 55·14, starch 100, saccharifiable cellulose 35·75, crude fibre 7·10, nitrogenous matter 69·06, undetermined constituents 51·15.

*Carrots.*—Digestive coefficients:—fat 56·3, sugar 100, saccharifiable cellulose 98·03, crude fibre 90·25, nitrogenous matter 89·28, pectic substances 100, undetermined constituents 90·88.

J. M. H. M.

**Composition and Methods of Analysis of Human Milk.** By A. R. LEEDS (*Chem. News*, 50, 263—267; 280—281).—The author has examined 84 samples of human milk, and has tested experimentally the various methods employed for the analysis of human milk. In the present communication the various methods previously employed are reinvestigated, and numerous sources of error pointed out.

He commends highly the Gerber-Ritthausen method (*Abstr.*, 1881, 657); it is the one employed in his analyses.

The 84 analyses of human milk are thus summarised. They had a uniformly alkaline reaction. Only normal milks were analysed after being submitted to a microscopical examination:—

	Average.	Minimum.	Maximum.
Specific gravity.....	1·0313	1·0260	1·0353
Albuminoids .....	1·995	0·85	4·86
Sugar .....	6·936	5·40	7·92
Fat .....	4·131	2·11	6·89
Solids not fat.....	9·137	6·57	12·09
Ash.....	0·201	0·13	0·37
Total solids (by addition of constituents) .....	13·268	10·92	16·79
Total solids (by evaporation). ..	13·267	10·91	16·66
Water.....	86·732	83·21	89·08

These results agree fairly well with those of earlier investigators of this subject. The most variable constituent of human milk is the albuminoid, the fat coming next, whilst the sugar is the least so.

The colour of the milk is no indication of its richness, the taste is usually more or less saline and somewhat disagreeable, whilst its consistency is much thinner and more watery than cow's milk. Although the amount of solids is greater in human than in cow's milk, nevertheless the specific gravities of the two classes of milk vary but

little one from the other, that of human milk being somewhat the greater. The milk from women under 20 years of age is richer in all respects than that from older women, and that of the first lustrum is richer in albuminoids, and especially in sugar than that of those succeeding it.

D. A. L.

**Relation of Phosphoric Acid to Nitrogen in the Urine during Feeding with Brain.** By G. POLITIS (*Zeits. f. Biol.*, 20, 193—214).

—Zülzer, Edlefsen, and others from their observations concluded that an increased excretion of phosphoric acid denoted an increased activity and decomposition of brain material. Voit, however, doubted the correctness of this conclusion, which is left in still greater doubt by the present experiments. A dog was fed for nine days on a meat diet consisting of 500 grams of cooked flesh, and the average relation of phosphoric acid to the nitrogen excreted was 1 to 6·7; on the 10th, 11th, and 12th days 50 grams of ox brain was included with the meat, its equivalent in meat being deducted, the relation however still remained the same. In another experiment the animal was fed on brain exclusively (518 grams per day); the urine during the day was analysed five times, at intervals of three hours, from 9 A.M. to 9 P.M., and not only did the average relation remain constant, but the relation was the same for the whole 24 hours. The reason of the varying relation during meat diet is owing to the fact that the phosphoric acid exists as inorganic salts (phosphates), which are easily absorbed and excreted; whilst in brain it exists in an organic combination, and consequently undergoes resolution concurrently with the proteid.

Moreover it seems unnecessary to attribute the increase, even admitting its truth, to increased activity of the brain solely, as that organ only forms  $\frac{1}{2}$  to 2 per cent. of the body weight, whilst the muscles, which themselves experience great activity, constitute 45 per cent.

J. P. L.

**Action and Fate of Trichlorethyl Alcohol and Trichlorobutyl Alcohol in the Animal Organism.** By E. KULZ (*Zeits. f. Biol.*, 20, 157—164).

—Liebreich incorrectly attributed the physiological action of chloral hydrate to the formation of chloroform in the organism, due to the alkalinity of the blood. Mering and Musculus found, however, a new body: “trichlorethylglycuronic acid,” excreted in the urine after taking chloral hydrate; this substance is *lævorotatory*, and is decomposed into trichlorethyl alcohol and *dextrorotatory* glycuronic acid when treated with mineral acids. The author has been unable to obtain this acid from the urine of patients kept under chloroform for a long time during operation, or from the urine of a dog continuously chloroformed for five hours. He further states that the *lævorotatory* action of the urine from chloroformed patients is due to the presence of a similar substance, “phenylglycuronic acid.” In the present paper, the author has given the results of experiments with trichlorethyl and trichlorobutyl alcohols; both produce a marked soporific effect and are excreted in the urine as their corresponding glycuronic acids. Both these latter compounds have still a very strong physiological action, producing a more prolonged sleep, although they take longer to produce

the effect than an equivalent dose of chloral hydrate, butyl-chloral hydrate, or trichlorethyl or trichlorbutyl alcohols. J. P. L.

**A New Lævorotatory Substance (Pseudohydroxybutyric Acid).** By E KULZ (*Zeit. f. Biol.*, 20, 165—178).—In the urine of diabetic patients taking chloral hydrate, after the sugar had been removed by fermentation, the author observed that the lævorotatory action of the urine in some cases exceeded that due to the trichlor-ethylglycuronic acid, and concluded that a second lævorotatory substance was present, which was incapable of precipitation either by lead acetate, basic acetate, or even basic acetate and ammonia. Neither was it identical with the lævorotatory body Haas has described as existing in normal human urine. In order to isolate this substance, one of the two following methods was adopted:—1st. After fermentation, the urine is concentrated and then precipitated with normal lead acetate, basic acetate, and basic acetate and ammonia; the filtrate freed from lead is evaporated to dryness, the residue dissolved in a little strong alcohol, and then absolute alcohol added until no more precipitate is formed. After remaining 24 hours, it is filtered and mixed with 5 times its volume of ether, whereupon the acid separates out as a light yellow syrupy mass. 2nd method. After fermentation, the acid liquid is concentrated to a syrup, and a large volume of ether added at once to separate the acid.

The purified acid was converted into its barium salt, and from this the potassium, magnesium, copper, cadmium, zinc, and silver salts were obtained; the last named crystallises in beautiful stellate needles, the elementary analysis of which agrees with the formula  $C_4H_7AgO_3$ , its specific rotatory power (using a Jellet-Cornu polarimeter) is  $[\alpha]_D = -8.637$ . The acid obtained by decomposing the silver salt with sulphuretted hydrogen forms a colourless syrup. Analyses of the acid and its silver salt gave numbers agreeing with the formula for a hydroxybutyric acid.

As however it does not agree in any of its properties with any of the four hydroxy-acids already known, the author has assigned to it the name of pseudohydroxybutyric acid; it gives no colour reaction with ferric chloride, and is not volatile with the vapour of steam.

In 52 cases under observation, the acid occurred only in the urine of the most severe, and of those which at the same time gave the ferric chloride reaction. It is besides of great clinical interest, for in one of the cases above mentioned, over 200 grams were eliminated in 24 hours; it may possibly too account for the lower percentages of sugar sometimes obtained by the polarimetric, than by the titrimetric method of estimation. J. P. L.

**Putrefaction of Albumin in the Alimentary Canal of Herbivora.** By L. BÖHM and O. SCHWENK (*Zeit. f. Biol.*, 20, 215—233).—The authors consider the negative results of both Brieger and Munk in their researches on oxen and horses, to be entirely due to the fact that they used too small a quantity to determine the presence of the volatile aromatic compounds of sepsis. They have therefore repeated the experiments, observing at the same time the same division

of the alimentary canal as Tappeiner did in his recent experiments on intestinal gases. The results, which are entirely of a positive character, are as follows:—Phenol is present in every section of the alimentary canal of both horse and ox; in the paunch and colon of oxen in sufficient quantity to be weighed as tribromophenol; indole in the small intestine of horses and oxen, in the cæcum of horses and in the cæcum and colon of oxen; skatole in the paunch of oxen and colon of horses. There can, too, be no doubt that they owe their origin to the sepsis of albuminous bodies in the intestine. About 10 per cent. of the proteïd of the food may approximately be considered as lost through putrefaction. In the horse, putrefaction begins earlier, as traces of phenol are evident in the stomach; in the colon it is more active than in any part of oxen; this is in agreement with the observations of Munk, namely, that more phenol was contained in horse's urine than in that of oxen. They do not consider the variation in behaviour of phenol when given to dogs and horses to be due to the greater power of oxidation in the blood of the latter, but to the fact that it is more slowly absorbed.

J. P. L.

**Anæsthetic Action of Cocaine.** By J. GRASSET (*Compt. rend.*, 99, 983—984).—When a 1 per cent. solution of cocaine hydrochloride is injected under the skin of dogs or monkeys, it produces complete cutaneous anæsthesia after some minutes, and this anæsthesia includes those muscles which lie nearer the surface, but there is a limit to the depth to which the effect extends below the skin.

C. H. B.

**Physiological Action of Dichloromethane compared with that of Chloroform.** By J. REGNAULD and VILLEJEAN (*Jour. Pharm.* [5], 9, 384—389).—The researches of the authors show (1) that the methylene chloride usually supplied to surgeons is simply a mixture, owing its anæsthetic properties to chloroform; (2) that the physiological action of dichloromethane is different from that of chloroform, and only resembles the latter in producing insensibility; (3) the symptoms produced by dichloromethane are constant, and of such a nature as to preclude the employment of this agent in surgery.

J. T.

**Analysis of the Contents of a Cyst formed under the Tongue.** By GUINOCHET (*Jour. Pharm.* [5], 9, 475—479).—The cyst was about 18 years growing, and weighed about 30 grams. Details of the method of analysis are given; its composition was found to be as follows:—

Soluble in ether..	{	water.....	21.20	}	74.73
		cholesterin .....	69.80		
		fatty matter.....	4.93		
Insoluble in ether	{	mineral salts.....	0.97	}	4.07
		blood, <i>débris</i> .....	3.08		
		albuminoïd matter			
					<hr/> 100.00

The large amount of cholesterin is very remarkable.

J. T.

**Occurrence of Xanthine, Guanine, and Hypoxanthine.** By A. BAGINSKY (*Zeits. Physiol. Chem.*, **8**, 395—403).—The researches of Fischer (Abstr., 1883, 354) having shown the close relation of xanthine to caffeine and theobromine, it appeared probable that it might occur in tea. The author, therefore, examined several samples of tea, and found not only xanthine, but also hypoxanthine.

A considerable quantity of the pancreas of the ox was divided into two portions. The first portion, examined whilst quite fresh, contained guanine 0·2797 per cent., xanthine 0·1145 per cent., hypoxanthine 0·128 per cent. The second portion was allowed to putrefy for three weeks, and then yielded guanine 0·0069 per cent., xanthine 0·0455 per cent., and hypoxanthine 0·0810. An experiment in which in the course of three days 4·28 grams of hypoxanthine was administered to a dog, showed that no increase was thereby caused in the amount of hypoxanthine excreted in the urine. In cases of acute inflammation of the kidneys in children, the urine contained quantities of xanthine varying between 0·0113 and 0·0285 gram per 100 c.c. of urine, whilst normal urine (of children) contains only 0·0028—0·003.

A. J. G.

**Guanine.** By A. KOSSEL (*Zeits. Physiol. Chem.*, **8**, 404—410).—The separation of guanine from hypoxanthine can only be effected by ammonia (in which guanine is sparingly, hypoxanthine readily soluble) in the absence of peptonous substances and many other compounds. It is therefore better to precipitate both substances together by means of ammoniacal silver nitrate, recrystallise the mixed silver salts from hot nitric acid in the presence of carbamide, and then, after removal of the silver, to effect a separation by ammonia. A loss of about 5·5 per cent. of the guanine is met with in this process, due to the solubility of guanine silver nitrate in the nitric acid employed. The amounts of guanine, hypoxanthine, and xanthine, in several animal tissues, &c., were determined with the following results, per 100 parts of the dry organ:—

	Guanine.	Hypoxanthine.	Xanthine.
Leuchæmic blood.....	0·201	0·072	Not determined.
Sarcoma of the peritoneum of a cow .	0·283	0·272	”
Sarcoma of the skin of the upper arm	0·196	0·137	”
Embryonal muscle (ox) .....	0·412	0·359	0·111
Muscle of adult animal (ox) .....	0·020	0·230	0·053
Muscle of adult animal (dog) .....	trace	0·222	0·093
Pancreas (ox I) .....	0·241	0·411	0·844
Pancreas (ox II) .....	0·746	0·364	0·130
Spleen (ox) .....	0·270	0·281	0·152
Liver (ox).....	0·197	0·134	0·121

A. J. G.

## Chemistry of Vegetable Physiology and Agriculture.

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**Chemistry of *Bacillus Subtilis*.** By G. VANDEVELDE (*Zeits. Physiol. Chem.*, **8**, 367—390).—These experiments were made to ascertain the changes produced by the growth of bacilli in solutions of extract of beef (containing 2.5, 5, and 10 grams of extract to 500 grams of water). The solutions were boiled in flasks closed by plugs of cotton-wool, or where the gases evolved were to be collected, placed with a little air, in tubes over mercury. After heating, the contents of each vessel were carefully seeded by the introduction of a few drops of a pure cultivation of *Bacillus subtilis*. Within 24 hours, the solution, originally clear, had become clouded, after a further 40—48 hours this cloudiness had vanished, and a bacillus-film of greyish-white colour had formed on the surface of the liquid. After awhile, this film broke up and sank in fragments to the bottom; sometimes one or more additional films formed in succession, but were so thin as to be nearly invisible, whilst bacilli were disseminated throughout the liquid, during these latter stages. The chemical examination of the liquids showed that ammonia and volatile fatty acids were formed at the expense of the creatinine and sarcolactic acid of the flesh extract; the formation of the fatty acids from the latter occurring especially in the latter period of the action, when the bacillus was acting as an anaerobic ferment.

In similar solutions, to which glycerol and some calcium carbonate were added, the formation of lactic, butyric, and a small quantity of succinic acid was noticed. The gas evolved in the earlier stage of fermentation contained carbonic anhydride 22.52 per cent., hydrogen 15.35, nitrogen 62.13; that evolved later contained carbonic anhydride 37.02, hydrogen 3.72, nitrogen 59.26; still later in the fermentation, carbonic anhydride alone was given off. Substituting grape-sugar for the glycerol, the formation of mannite, lactic acid, butyric acid, and (doubtfully) of caproic acid, was observed. Two alcohols were also formed, one boiling above and one below 100°, the quantity obtained was, however, too small for identification. The formation of succinic acid was also observed in one case. An analysis of the gas evolved in the later stage of the fermentation gave carbonic anhydride 78.61, hydrogen 3.39, nitrogen 18.00. Samples of gas from still later stages consisted of carbonic anhydride with traces of hydrogen.

A. J. G.

**Sterilisation of Fermentable Liquids in the Cold.** By A. GAUTIER (*Bull. Soc. Chim.*, **42**, 146—150).—The filter used by the author to sterilise liquids in the cold, consists of a small flask of biscuit porcelain or faience, with a long and narrow neck. A glass tube passes down the neck to the bottom of the flask, and is cemented into the neck by means of a lead borosilicate. This cement is made by melting together boric anhydride 8 parts, silica 2 parts, red lead 12 parts, and allowing the mass to cool. It is then powdered very

fine, mixed with terebenthene to form a paste, applied to the joint, and heated to redness. This cement is elastic, very fusible, and can be applied to glass, porcelain, faience, &c.

The receiver for the sterilised fluid consists of a glass flask with a narrow neck, which carries a tube bent at right angles and reaching to the bottom of the flask, and another side tube which is connected with the pump. The tube which passes to the bottom of the receiver is ground to fit that which passes to the bottom of the filter, and the two are thus connected. Between the receiver and the pump is a cylinder packed with asbestos. The filter and receiver are sterilised by heat, connected together, the filter placed in the particular liquid, and the receiver rendered vacuum. The liquid passes through the porous walls of the filter and thence into the receiver. Diastatic granules, ferments, &c., are deposited on the external surface of the filter, but the latter can be readily sterilised by heating it in a Bunsen flame.

In this way solutions of egg albumin, blood serum, grape juice, peptones, milk, &c., can be sterilised without the application of heat. As a rule, acid liquids treated in this way may be kept indefinitely without undergoing any change, but alkaline liquids sometimes become turbid after a time, but give off no gas or odour, and eventually become clear again and undergo no further change.

Albumin solutions, after filtration in this way through biscuit porcelain, are not coagulated by heat, nor by carbonic, acetic, or nitric acid in the cold. The hot solution coagulates in presence of nitric acid, but not in presence of acetic acid. If the albumin solution is heated to 100°, allowed to cool, and then treated with a current of carbonic anhydride, it yields a precipitate which dissolves if the passage of the carbonic anhydride is continued, or if air or oxygen is bubbled through the liquid. The solution thus formed is not coagulated by acetic acid in the cold in presence of sodium phosphate, but coagulates when heated under these conditions.

Dilute solutions of casein seem to behave in the same way, and it is evident that if these liquids are thus modified by filtration through biscuit porcelain, they may undergo much greater changes by filtration across vegetable or animal membranes. C. H. B.

**Employment of Plaster Filters to Sterilise Liquids.** By P. CAZENEUVE (*Bull. Soc. Chim.*, 42, 89—94).—Pasteur has adopted a filter of plaster of Paris to separate the bacteria of Davaine in the charbon disease. As Benoist and Miquel have pointed out that these filters possess the disadvantage of depositing traces of calcium sulphate in the filtrate, which exerts a certain antiseptic action, the author has submitted them to a more critical observation. Milk, blood, bile, and albuminous urine were completely deprived of the albumin on filtration, this effect being due partly to a chemical combination of the calcium sulphate with the albumin, and partly to the retention of the latter in the capillaries of the filter. But after a time these become more or less choked, the filtration is retarded, and the albuminous substances pass through.

It is here shown by a series of experiments that these filters retain soluble or diastatic ferments, such as the diastase of malt, the myrosin



of mustard, the synaptase of almonds, pepsin, and the diastase of *Torula urinæ*.

Pasteur has observed that the liquid obtained by filtering the blood in the charbon disease, loses its virulence from the separation of the bacteria, which act by virtue of their physiological action, namely, their avidity for oxygen. But this explanation is here criticised as insufficient, and judging from the above experiments, improbable; it is here suggested that the bacteria owe their virulence to the production of a diastatic action. This latter is prevented by the process of filtration.

V. H. V.

**Action of Various Compounds on Bacteria of the Genus *Tyrophthrix* and their Spores.** By CHAIRY (*Compt. rend.*, 99, 980—983).—The author has estimated the amount of various solutions (viz., sulphuric acid, chlorine-water, sulphurous acid, hydrogen sulphide, alcohol, phenol, zinc chloride, alkaloids) required to maintain the transparency of solutions of animal matter when inoculated with various species of *tyrophthrix*, and also the quantities required to kill the spores of these bacteria. He has also examined the action of various gases on the spores, the latter being collected on filter-paper, dried by exposure to air, and then subjected to the action of the gas.

The nature of the liquid to which the bacteria are added, has very little influence on the quantity of a substance required to prevent the development of the spores or to kill them. The influence of the mass of bacteria present in the liquid is, however, very marked. Those compounds which have a pronounced acid character (e.g., sulphuric acid, chlorine-water, hydrogen sulphide) exert the most destructive action on the bacteria and their spores, whilst substances like alcohol and the alkaloids are efficient only when present in relatively considerable quantity. It is worthy of note, in connection with this result, that the development of the bacteria tends to make the liquid alkaline.

The action of gases on the spores depends on the acid character of the products to which they give rise, and the behaviour of these products towards the envelopes of the spores. Nitrogen peroxide is more active than chlorine, which in its turn is far more active than sulphurous anhydride or hydrogen sulphide. The two latter do not kill the spores but simply delay their development. Ozonised air, containing 3—4 per cent. of ozone, has no appreciable effect on the spores.

C. H. B.

**Activity of Assimilation by Leaves.** By J. SACHS (*Ann. Agronomiques*, 10, 514—517; from *Bot. Zeit.*, 1884, 428).—By the use of a colorimetric method depending on the various tints assumed by leaves when stained with iodine in a certain manner, the author has investigated the rapidity of formation and disappearance of starch under various circumstances, and in many different species of plants. He estimates that a square metre of leaf, during a favourable day (24 hours), produces about 24 grams of starch, to which must be added nearly a gram lost by respiration.

J. M. H. M.

**Formation of Albumin in Green Plants.** By A. EMMERLING (*Landw. Versuchs-Stat.*, 31, 182—183).—Previous observations on the

presence of amido-acids in all parts of green plants, have left the question undecided, whether they are formed by synthesis in the assimilating organs, or are derived from the decomposition of albumin already formed in the plant. The author has made fresh experiments to decide the question by examining the various forms of nitrogen present in the experimental plants—*Vicia faba*—in different stages of their growth. The results of his experiments are in favour of the former hypothesis, namely, that it is a synthetic process. The process begins with the formation of the roots, and afterwards of the leaves; when these are perfected, the amido-acids accumulate in the fruits and assist their rapid development. The probability of this first hypothesis is rendered greater, when the difficulty of explaining the known facts by the second is considered; the amido-acid being found in the youngest leaves is opposed to the probability of the decomposition theory, whereas the synthetic process is harmonious and only requires the supposition of one regular process during the whole growth of the plant. J. F.

**Fat in Palm Nuts.** By V. v. WILM (*Landw. Versuchs-Stat.*, **31**, 202—204).—The ordinary method of extraction by Soxhlet's apparatus does not remove all the fat from palm nuts in the time (3—3½ hours) usually employed with other substances, a second extraction yielding another 1 per cent.; other feeding stuffs yield their fat to within a minute fraction of 1 per cent. The matter is of considerable importance, as in recent times the palm nut cake or meal has been more thoroughly deprived of oil than formerly, the average of fat being 3—5 per cent.; so that 0·5—0·7 per cent. is an important figure in an analysis. The suggestion was made that the substance obtained by the second extraction is not true fat, but a species of wax; tested by appearance, smell, melting, and solidifying points, it, however, proves to be a true fat. Thinking that the fat cells of the palm nut are of a dense nature and do not permit the ether to have free access to the fat, the author ground samples of the substance to different degrees of fineness, and extracted the fat in the usual way; the results showed the correctness of his views, the coarser samples leaving a large proportion untouched, whilst all the fat was obtained from those finely ground. J. F.

**Oleaginous Seeds of the *Symphonia Fasciculata* (Clusiaceæ).** By J. REGNAULD and VILLEJEAN (*Jour. Pharm.* [5], **10**, 12—16).—The authors give a detailed account of the analyses of these seeds from Madagascar. They remark that—(1.) The analyses of the seeds are very interesting on account of the large amount (56 per cent.) of fatty principles not containing any substance susceptible of modifying their mild taste, and remarkable for the nature of the glycerides present, and their striking analogy to the glycerides of the mammalia employed as food. (2.) The astringent matters isolated are very similar to those of the cinchona, ratanhia, &c. (3.) Besides quercetin they have only found cellulose, and pectous and albuminoid bodies, such as occur in analogous vegetable organs. J. T.

**Occurrence of Phytosterin.** By H. PASCHKIS (*Zeits. Physiol. Chem.*, 8, 356—357).—The author has obtained from colchicum seeds a substance agreeing in properties with phytosterin, the homologue (?) of cholesterol previously observed in Calabar beans by Hesse (*Abstr.*, 1878, 850), and in peas by Kolbe. A. J. G.

**Composition of Maize.** By SCHICHOWSKY (*Ann. Agronomiques*, 10, 518—519).—300 grams maize grains contain 260 grams dry matter, apportioned as follows: envelope 17 grams, albumin (botanical) 216 grams, embryo 27 grams. The embryo is richest in minerals and the envelope poorest, the ash per cent. of dry matter being in the envelope 1·71, albumin 0·36, embryo 8·23. The envelope ash contains about 23·5 per cent. each of sulphuric and phosphoric anhydrides; the albumin ash contains 36·4 P<sub>2</sub>O<sub>5</sub> and 14·4 SO<sub>3</sub>; and the embryo ash 41·8 P<sub>2</sub>O<sub>5</sub> and 19·4 SO<sub>3</sub>. Lime and magnesia are very unequally distributed. The envelope ash contains 10·5 MgO and 2·3 CaO; the albumin ash 8·5 MgO and 0·06 CaO; the embryo ash 6·6 MgO and 7·9 CaO. The albumin is richest in alkalis, then the envelope, lastly the embryo. Silica is contained in the following proportions: envelope ash 5·5; albumin ash 1·4; embryo ash 0·2; the distribution of the iron is like that of the silica. No part of the grain contains chlorine.

J. M. H. M.

**Composition of the Food of Scotch Hill Sheep.** By E. KINCH (*Trans. Highland and Agric. Soc.*, 16, 273—280).—The author has executed analyses of the species of grasses and other forage plants collected in May and June, 1883, from the hill pastures of Auchenbrach. The results are given in the following table; in addition to the determinations of albuminoids made by Church's phenol process, duplicate determinations were made by the copper hydroxide process; these latter gave in all cases results slightly higher than the former:—

*Composition of Fresh Plants.*

	Moisture.	Ash.	Nitrogen × 6·25.	Fibre.	Ether extract.	Non-nitrogenous extractive matter (by difference).	Albuminoids by phenol method.	Albuminoids by copper hydrate method.
<i>Aira cæspitosa</i> .....	69·18	1·80	4·40	9·04	1·14	14·44	3·77	3·97
<i>Molinia cærulea</i> .....	69·82	1·28	6·19	9·25	0·98	12·48	4·83	5·02
<i>Nardus stricta</i> .....	56·58	2·37	6·05	13·52	0·63	20·85	4·15	4·37
<i>Carex cæspitosa</i> .....	68·26	1·60	6·20	8·39	0·93	14·62	5·53	5·59
<i>Carex panicea</i> .....	67·73	1·95	6·49	7·24	1·18	15·41	5·63	5·75
<i>Eriophorum vaginatum</i>	74·46	0·83	3·51	8·17	0·18	12·85	3·40	—
<i>Scirpus cæspitosus</i> .....	68·52	1·18	4·89	8·38	0·97	16·06	3·28	3·56
<i>Juncus articulatus</i> .....	82·09	1·44	2·45	4·82	0·19	9·01	—	—
<i>Juncus squarrosus</i> .....	75·95	1·39	2·62	7·25	0·24	12·55	2·19	2·25
<i>Erica vulgaris</i> .....	65·43	1·12	3·13	7·52	2·87	19·93	2·66	—

*Composition of Dry Matter.*

	Ash.	Nitrogen $\times 6.25$ .	Fibre.	Ether extract.	Non-nitrogenous extractive mat- ter.	Albuminoids by phenol method.	Per cent. of nitrogen, albuminoid.	Per cent. of nitrogen, non- albuminoid.
<i>Aira cæspitosa</i> .....	5.86	14.12	29.26	3.72	47.04	12.25	86.73	13.27
<i>Molinia cærulea</i> .....	4.24	20.50	30.65	3.25	41.36	16.00	78.05	21.95
<i>Nardus stricta</i> .....	5.46	13.93	31.13	1.46	48.02	9.56	68.61	31.39
<i>Carex cæspitosa</i> .....	5.04	19.56	26.43	2.92	46.05	17.43	89.14	10.86
<i>Carex panicea</i> .....	6.04	20.12	22.42	3.68	47.74	17.57	86.84	13.16
<i>Eriophorum vaginatum</i>	3.26	13.75	31.99	0.73	50.24	13.35	97.09	2.91
<i>Scirpus cæspitosus</i> ....	3.75	15.58	26.61	3.09	50.99	10.44	66.99	33.01
<i>Juncus articulatus</i> ....	8.08	13.68	26.90	1.04	50.30	—	—	—
<i>Juncus squarrosus</i> ....	5.77	10.90	30.17	0.99	52.17	9.12	83.69	16.31
<i>Erica vulgaris</i> .....	3.24	9.06	21.74	8.33	57.63	7.69	84.83	15.17

J. M. H. M.

**Composition of Inferior Hay.** By A. MORGEN (*Landw. Versuchs-Stat.*, 31, 204—205).—Two samples of hay were submitted to the author, from a farm on which the cattle were very subject to weakness and fracture of the bones. He found No. 1 to contain only 0.37 per cent. of lime and 0.20 per cent. phosphoric acid. The botanical examination showed that it consisted of so-called acid grasses and weeds, and contained few of the more nutritive grasses. Sample No. 2 contained 0.67 lime and 0.26 phosphoric acid; there was also a large proportion of the better grasses present. The albumin was estimated in both samples, but the author thinks, with A. Meyer, that the lime and phosphoric acid are of greater importance. J. F.

**Analysis of White Carrot Fodder.** By G. KRECHEL (*Jour. Pharm.* [5], 9, 28—33).—The author had occasion to analyse some samples of white carrot grown near Corbeil in a clayey calcareous soil manured with farmyard manure. The root only was taken, the tops having been removed, and was found to contain—

Water .....	85.727
Sugar .....	10.400
Starch .....	0.351
Cellulose .....	0.850
Pectic acid .....	1.990
Proteid matter.....	0.077
Mineral constituents.....	0.846

100.241

Deduct oxygen for the chlorine.. 000.004

100.237

## Mineral constituents (directly 0·828).

Silica.....	0·205	Chlorine.....	0·019
Iron .....	0·002	Carbonic anhydride ..	0·132
Lime .....	0·012	Sulphuric anhydride .	0·042
Magnesia ....	0·011	Phosphoric anhydride	0·108
Potash .....	0·238		
Soda .....	0·077	Total .....	0·846

Organic acids, resinous and fatty matter not estimated.

The ash contains—

Silica.....	25·40	Potash .....	29·50
Iron .....	0·31	Soda.....	9·55
Lime.....	1·50	Chlorine ....	2·42
Magnesia....	1·40		

Carbonic anhydride .....	16·40
Sulphuric „ .....	5·20
Phosphoric anhydride .....	13·40

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104·08

Deduct oxygen for chlorine..... 0·55

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103·53

In beetroot it has been repeatedly observed that the phosphoric anhydride is present to the extent of 1·1 per cent. of the sugar found ; in this root, the proportion is 1·04 per cent. The sugar was estimated by Fehling's solution, the pectic acid by Schloesing's method. Starch was estimated in the residue from the preceding by digesting it with very dilute sulphuric acid, and determining the sugar produced. The pulpy residue was washed successively with acid and potash, then with water, and assumed to be cellulose. J. T.

**Vegetation of the Sugar-beet in the Second Year.** By H. LEPLAY (*Compt. rend.*, 99, 1030—1031).—The sugar in the root of the beet at the commencement of the second year continually diminishes up to the maturity of the seed, at which point it has completely or almost completely disappeared. Six weeks before maturity (about the middle of July) the stalks, leaves, and green seeds contain no sugar. The density of the sap diminishes in the root and increases in the stalks, then in the leaves, and finally in the seeds in the proportions respectively of 2, 2·7, 3·4, and 4·2. Potassium salts of vegetable acids exist in the juice in all parts of the plant, but the amount in the root is almost double what it was at the end of the first year. Soluble and insoluble calcium compounds exist equally in all parts of the plant. The tissues of the ascending axis of the beet in the second year seem to contain more calcium in insoluble organic combination than the same tissues in the first year, with the exception of the stalks, which contain less than the petioles of the first year. The green

seeds also contain a somewhat large quantity of lime in insoluble organic combination. In the beet in the second year, there is an ascensional movement of the calcium and potassium compounds from the soil to the leaves and to the grains, similar to that observed in the maize plant during the formation of the grain (Abstr., 1883, 366). In this movement, the bicarbonates and carbonic acid absorbed from the soil by the root undergo organic transformation as in the first year. Potassium and calcium salts of organic acids are not wholly retained by the root, but are distributed throughout the ascending axis, and especially in the leaves and seeds. The movement of the calcium towards the leaves and the seeds is very strongly marked. The potassium and calcium compounds contained in the root of the beet in the first year are not nearly sufficient to meet the requirements of the plant in the second year, and the quantity of these bases absorbed from the soil in the second year is ten times as great as that existing in the root in the first year. The potassium and calcium salts existing in the juice in various parts of the beet seem to have the same ultimate functions as in the maize plant (*loc. cit.*); the potassium salts contribute to the formation of the seeds, and the calcium salts to the formation of the tissues.

C. H. B.

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## Analytical Chemistry.

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**Microscopic Chemical Reactions.** By A. STRENG (*Jahrb. f. Min.*, 1885, 1, Mem., 21—42).—The author, from the frequent application of chemical methods in the examination of rocks, is enabled to improve and simplify the methods of microscopic chemical research. It must, however, be remarked that considerable skill and practice are required in all these methods.

*Phosphoric Anhydride.*—In 1876, the author proposed to determine the phosphoric anhydride in apatite, under the microscope, by means of a nitric acid solution of ammonium molybdate. To the application of this reagent, Stelzner objected, as soluble silicates may give a similar reaction. The author has thoroughly examined the matter, and finds that it is always apatite which occasions the precipitation of the yellow granules, but that the amount of the precipitate is greatly increased by the presence of soluble silica, so that one can be led to believe that the whole silicate consists of apatite, whereas the latter is present only in very small quantity. In order to detect the presence of apatite in a section with certainty, even in the presence of soluble silicates, the crystal to be tested for phosphoric anhydride is isolated by a glass cover, in which a hole is bored. The crystal is then dissolved in a drop of concentrated nitric acid, evaporated at a gentle heat, the residue decomposed with water, the solution removed by a pipette, placed in three drops on a glass and evaporated to dryness.

The first residue is then treated with a drop of molybdate solution, and observed under the microscope. If a number of rhombic dodecahedra and octahedra are rapidly precipitated, phosphoric anhydride is present. Silica in this case cannot act, as it is rendered insoluble by the evaporation. The second residue is decomposed by a drop of dilute sulphuric acid. If needles of gypsum are formed, lime is present. The third residue may be tested for sodium. The magnesium ammonium chloride, suggested by Behrens as a test for phosphoric anhydride, gives very good results, but is not so delicate as the molybdate test.

*Potassium.*—As a test for potassium, Behrens has suggested platinum chloride. The crystals of potassic platinochloride frequently occur as cubes, with or without rhombic dodecahedra and octahedra. Full details are given for performing the test.

*Sodium.*—The author has suggested a reaction (Abstr., 1884, 366) of a very delicate nature. The reagent is uranium acetate.

*Lithium.*—Various reagents have been proposed as microscopic tests for lithium; the best is potassium carbonate. The author has also endeavoured to employ sodium lithium phosphate, but further experience is necessary before an opinion can be given as to its merits.

*Calcium and Strontium.*—As a good microscopic reagent for calcium, dilute sulphuric acid has long been employed. Another method is to use a concentrated solution of oxalic acid, distinct octahedra being formed. Exactly the same reaction is given by strontium with oxalic acid. Were it necessary to detect strontium and calcium together, it could be done with dilute sulphuric acid.

*Barium.*—A good microscopic reagent for barium is potassium ferrocyanide. If a drop of warm dilute barium chloride is mixed with a drop of potassium ferrocyanide, allowed to cool, and diluted, yellow rhombohedra of barium ferrocyanide separate out. Witherite and strontianite may be easily distinguished, if the dilute hydrochloric acid solution is divided into two drops, one treated with potassium ferrocyanide, and the other with oxalic acid. Witherite in the first shows yellow octahedra, strontianite in the second colourless octahedra.

*Magnesium.*—Sodium phosphate, recommended by Haushofer and Behrens, is very suitable for microscopic work. The author finds that the best crystals are obtained when ammonia is added to the sodium phosphate, and ammonium chloride to the solution to be tested; the drops of both solutions are heated to 100°, then mixed, and cooled slowly.

*Aluminium.*—As a test for aluminium, hydrogen potassium sulphate may be employed. A more delicate test is cæsium chloride, as cæsium alum is more insoluble than potassium alum. B. H. B.

**Detection of Iodine, Bromine, and Chlorine.** By E. HART (*Chem. News*, 50, 268—269).—The substance is boiled in a flask with a solution of ferric sulphate, a suitable bent tube with bulbs containing starch-paste having been previously attached to the flask



by means of a perforated cork. The presence of iodine is indicated by the production of the usual blue coloration; the bulbs are of course kept cool. When all the iodine is thus driven off, chloroform is substituted for the starch-paste in the bulbs, and a small quantity of permanganate added to the contents of the flask, which is again boiled; the presence of bromine is shown by the usual coloration of the chloroform. After all the bromine is eliminated, chlorine can be tested for in the solution in the ordinary way. This method has been tested experimentally and gives satisfactory results. D. A. L.

**Estimation of Iodine in Urine.** By E. HARNACK (*Zeits. Physiol. Chem.*, 8, 391—394).—A reply to E. Baumann (*ibid.*, Part IV).

**Estimation of Sulphurous Anhydride.** By C. L. REESE (*Chem. News*, 50, 218).—The sulphurous anhydride solution, contained in a stoppered bottle, is titrated with a solution of hydrogen peroxide of known strength. A few drops of titanium sulphate solution are added to act as an indicator, a permanent yellow colour showing when the titration is complete. Results are low with this method. The hydrogen peroxide solution is standardised by means of permanganate. D. A. L.

**Estimation of Alkalis in Silicates.** By T. M. CHATARD (*Chem. News*, 50, 279).—This is an improvement on Hempel's process (*Abstr.*, 1882, 552).—The finely powdered mineral is mixed with twice its weight of bismuth oxide, placed in a platinum crucible, and heated, at first gently, then gradually to full redness, at which it is kept for ten to fifteen minutes; decomposition is complete when the solid mass is perfectly friable. When cool, it is transferred to a dish and treated with hydrochloric acid, and if a complete analysis is required the silica and then the bismuth are removed in the usual way. If alkalis only are to be determined, ammonia and ammonium carbonate are added, and the removal of magnesium and the alkali determinations are proceeded with in the ordinary way. The process gives good results. The more basic the silicate, the less likely is it to fuse when heated with the bismuth oxide, and *vice versa*; therefore, to prevent the fusion of acid silicates, and ultimately to get them in the very convenient friable condition, it is advantageous to add an equal weight of calcium carbonate as well as the bismuth oxide before heating. D. A. L.

**Volumetric Estimation of Calcium Oxide and Carbonate.** By PRUNIER (*Jour. Pharm.* [5], 9, 300—303).—On titrating a solution containing calcium salts with a standard solution of ammonium oxalate, the precipitate formed does not settle quickly enough to give good results. The author finds that a sufficiently rapid deposition of the precipitate takes place if a little starch is added to the solution after it has been neutralised with pure ammonia, and the mixture is boiled. The solution of oxalate can be standardised with pure calcium carbonate, dissolved in dilute hydrochloric acid, neutralised with ammonia free from carbonate, and boiled with a little starch. The solution is heated from time to time, and allowed to stand one or

two minutes for the precipitate to settle. If a persistent froth forms on the surface, a few drops of strong alcohol are added, and the upper portion of the liquid is heated. Results are accurate to  $\frac{1}{2}$  per cent.

J. T.

**Estimation of Iron by Potassium Permanganate in Presence of Free Hydrochloric Acid and Chlorides.** By J. J. HOOD (*Chem. News*, 50, 278).—It is well known that the titration of iron by means of permanganate is untrustworthy in the presence of free hydrochloric acid, owing partly to the action of the acid on the permanganate, and partly to the yellow colour acquired by the solution. The author has observed that the presence of many soluble chlorides also produces an error in such estimations, and suggests the addition of a few c.c. of a strong solution of magnesium sulphate (1 or 2 grams according to the amount of chloride present) to the iron solution before titration. The titration can then be conducted just as accurately as if sulphuric acid had been used instead of hydrochloric acid, or as if no chlorides were present.

D. A. L.

**Estimation of Antimony.** By G. T. DOUGHERTY (*Chem. News*, 50, 278).—The following method is recommended for the approximate estimation of antimony in ores, hard leads, antimony slags, &c.:—About 10 grams of the substance are employed. If oxides are to be assayed, they are reduced to a metallic button by charcoal or red argol; if sulphur is present, a mixture of equal parts of potassium cyanide and sodium carbonate should be used for the decomposition. The metallic button is weighed, cut into small pieces or hammered out thin, and boiled with nitric acid, diluted with an equal volume of water, until the alloy is decomposed. The solution is diluted, the antimony tetroxide filtered off, dried, ignited, and weighed. The lead may be obtained by difference if the button was pure, or may be determined as sulphate in the solution.

D. A. L.

**Detection of Cyanogen.** By A. VOGEL (*Chem. News*, 50, 270).—The reaction of hydrocyanic acid with trinitrophenol is recommended; 1 in 30,000 can be detected, and the reaction is considerably more rapid than the formation of Prussian blue. The trinitrophenol should be neutralised by heating with soda or potash solution before employing it for this test, otherwise the darkening of the colour of the trinitrophenol when heated with alkali might lead to an error of judgment.

The substance to be tested is treated with soda solution, then boiled with the neutralised picric acid; the appearance of a deep red colour indicates the presence of hydrocyanic acid. By this means hydrocyanic acid has been detected in tobacco smoke and coal gas.

D. A. L.

**Ammonia, Nitrous Acid, and Nitric Acid in Potable Waters.** By GREINERT (*Chem. News*, 50, 279).—The author remarks that out of 126 waters examined, 21 contained ammonia alone, 6 nitrous acid alone, 35 nitric acid alone, 15 nitrous and nitric acid, 13 nitrous acid and ammonia, 17 nitric acid and ammonia, 19 nitrous and nitric acid and ammonia, and complains that the present theory of

the conversion of ammonia into nitric acid does not explain either the appearance of nitrous acid without ammonia, or the appearance of ammoniacal compounds along with nitrates without any nitrites.

D. A. L.

*Note by Abstractor.*—A full explanation of phenomena such as are described above will be found in Warington's paper on Nitrification (*Trans.*, 1884, 637—672). The first difficulties are explained on p. 639, where it is shown that the character of the organism determines the production of either nitrites alone or nitrates alone, whilst the total removal of ammonia is ensured when all conditions are favourable for nitrification.

D. A. L.

**Separation and Estimation of Methyl Alcohol in Presence of Ethyl Alcohol.** By C. DE PONCY (*Dingl. polyt. J.*, **254**, 500).—Both alcohols combine readily with oxalic acid in the presence of gaseous hydrochloric acid. Methyl oxalate is readily soluble in water, ethyl oxalate, however, is only sparingly soluble; by dissolving the two ethereal salts in water or alcohol, and treating with ammonia, insoluble amides are formed, a circumstance on which the determination of the methyl alcohol is based.

10·8 grams of oxalic acid are dissolved in 10 c.c. of the alcohol to be examined, and the solution is saturated with hydrogen chloride. The mixture is allowed to stand for 24 hours in a well-closed flask, after which 2 c.c. are diluted with 10 c.c. of water and filtered. Methyl oxalate being completely soluble in water, the quantity of oxamide produced on adding ammonia to the aqueous solution will be greater than that from an equal amount of ethyl oxalate. The quantity of oxamide formed in the washings of the ethyl oxalate may be determined by a series of trials. For pure alcohol, the average is 6·6 per cent. For methyl oxalate, the number is between 14·65 and 15 per cent. of the quantity of methyl alcohol. If instead of pure alcohol a mixture of ethyl and methyl alcohol is employed, the quantity of methyl alcohol can be calculated from the oxamide found. For every per cent. of methyl alcohol, 0·14 to 0·15 per cent. more than 6·6 per cent. is obtained.

D. B.

**Detection of Coal-tar Colours in Wines by Means of Ammonia and Amyl Alcohol.** By JAY (*Bull. Soc. Chim.*, **42**, 166—167).—In testing for coal-tar colours in wines by the ordinary method of adding ammonia to alkaline reaction and shaking with amyl alcohol, it is necessary to avoid a great excess of ammonia, and the proportion of the latter should never be more than 3 per cent., for if this is exceeded, the amyl alcohol may remain colourless, even if the wine contains a coal-tar colour. If the amyl alcohol is colourless it should be decanted off, filtered, and evaporated with a small quantity of silk, when the foreign colouring matter, if present, will become fixed on the silk.

C. H. B.

**Analysis of Red Wine by Means of Electrolysis.** By L. M. KROHN (*Jour. Pharm.* [5], **9**, 298—300).—If an electric current, say

from a couple of Bunsen cells, be passed through 5 to 10 c.c. of natural red wine diluted with 6 volumes of water acidified with some drops of sulphuric acid, a red lamellar deposit soon forms on the positive pole. It is quite visible to the naked eye, whilst under the microscope it appears as a tissue. After 12—20 hours it is quite compact. During the passage of the current, the odour of aldehyde is perceptible; the red liquid gradually becomes yellow, and finally colourless. White wines similarly treated lose their faint colour, but give no deposit. On isolating the red colouring matter of wine by means of lead acetate, and redissolving the precipitate in alcohol and a little tartaric acid, the deep red solution gives the same red deposit at the positive pole. The colouring matters usually employed for the adulteration of wine do not give this deposit, although they are decolorised, so that electrolysis combined with a microscopic examination of the deposit formed affords a certain means of ascertaining whether the colour of a red wine is natural.

J. T.

**Estimation of Starch in Gluten Bread.** By L. RICHARD (*Jour. Pharm.* [5], 9, 27).—Direct saccharification gives results which are too high, owing to the conversion of other principles always present in gluten bread. It is therefore necessary to isolate the starch. The gluten is finely powdered, washed well with water, until the wash-water carries off no more starch. The washings containing the starch are evaporated to a small bulk, mixed with sufficient sulphuric acid, and heated at 105° for 10 hours in a sealed glass tube. The glucose formed is then estimated in the neutralised liquid.

J. T.

**Estimation of Gum Arabic in Syrup.** By A. ANDOUARD (*Jour. Pharm.* [5], 9, 18—19).—The author points out defects in Roussin's method of coagulation by ferric sulphate, and in Soubeiran's method of precipitation by alcohol. The defects of the latter method are obviated by slightly acidifying the alcohol employed. The author recommends the following process:—Gradually dilute 10 grams of the syrup with 100 c.c. of alcohol at 85°, add 20 drops of acetic acid, and stir vigorously. After standing about three hours, pour on to a double tared filter, when the gum forms a cake which easily drains. Dissolve in 7—8 c.c. water and repeat the precipitation, collect on the filter before used, after washing by decantation with pure alcohol, and wash on the filter with the same alcohol. Dry at 100° and weigh. Afterwards, as Soubeiran suggests, expose to the air for 24 hours and weigh again, when the gum will have taken up its normal amount of moisture. The results are very exact. This method is not applicable to a product containing gum and commercial glucose, although it serves to detect the latter when alone. This gives a turbidity with alcohol due to the precipitation of dextrin, which may be taken for gum arabic at the first glance, but the dextrin forms a glue-like mass on the sides of the vessel. Further tests readily show whether the precipitate is gum or dextrin.

J. T.

**Milk Adulteration.** By SAMBUC (*Jour. Pharm.* [5], 9, 95—101).—The author published in 1879 a simple method of detecting

the addition of water to milk. The method requires from 10—20 minutes, and it consists in coagulating by an acid, and determining the sp. gr. of the serum after filtration. This is sufficiently constant in unadulterated milk to afford a ready means of detecting the addition of water. 150 c.c. of milk are warmed to 40—50°, and 10 c.c. of an alcoholic solution of tartaric acid of sp. gr. 1·030—1·032 (prepared with alcohol of 85°) are added. The mixture is taken from the fire and agitated with a small bundle of twigs, and the serum is passed through a linen filter; a slight turbidity in the filtrate does not appreciably affect the result. After cooling to 15°, the sp. gr. is taken with a lactometer. Numerous experiments made in the spring of 1879 at Rochefort, and in October and November of last year at Toulon, show that the sp. gr. of serum thus obtained never falls below 1·0278. All milk giving a serum sp. gr. of 1·024—1·025 ought to be regarded as falsified with at least one-tenth of water; a sp. gr. of 1·021—1·022 would indicate two-tenths, or each tenth of water lowers the reading by 3° to 3·25° of the lactometer. J. T.

**Koettstorfer's Method for the Examination of Butter for Foreign Fats.** By R. W. MOORE (*Chem. News*, 50, 268).—The author has examined, by the Koettstorfer and the Reichert methods, numerous vegetable oils and some mixtures in order to ascertain which, if any, could be used, without detection, for the adulteration of butter or oleomargarine. The results are:—

Kind of oil.	Mgrms. KHO required for 1 gram of oil.	c.c. $\frac{N}{10}$ NaHO, for 1 gram of oil.
Olive .....	185·2	0·2
Cotton seed.....	191·2	0·3
Pea nut .....	196·6	0·4
Palm .....	196·3	0·8
Beune .....	192·4	0·6
Sweet almonds ....	187·9	0·3
Poppy .....	192·8	0·5
Rapeseed.....	183·0	0·3
Linseed .....	195·2	0·2
Cocoa butter ....	199·8	1·6
Cocoonut.....	250·3	3·7
„ washed ...	246·2	2·7

Koettstorfer fixes between 221·5 and 232·4 mgrms. KHO as the limits of the amount required to saponify 1 gram of real butter. Of the above oils, cocoonut oil alone exceeds these limits. The washed cocoonut oil was treated with large quantities of boiling water to free it from fatty acids. The following mixtures were then examined, 1 gram of the oleomargarine requiring 193·5 mgrms. KHO.

Cocoonut oil.	Oleomargarine.	Mgrms. KHO per gram.	Washed oil.	Oleomargarine.	Mgrms. HKO. per gram.
49·3 p.c. 70·2 „	50·7 p.c. 29·8 „	220·0 234·9	53·1 p.c. 75·9 „	46·9 p.c. 24·1 „	223·6 234·9

Koettstorfer's method evidently does not detect the admixture, nor is it probable that Hehner's method would do so, since the cocoonut oil yields 86·43 per cent. of insoluble fatty acids. Reichert's method, on the other hand, shows the adulteration, as genuine butter would require more than three times as much  $\frac{N}{10}$  NaHO as the mixture.

D. A. L.

**Detection of Cotton-seed Oil in Olive Oil.** By BECHI (*Jour. Pharm.* [5], 9, 35—36; from *Jour. Pharm. d'Alsace-Lorraine*).—The methods proposed up to the present time are unsatisfactory. The author finds the following to give good results:—5 c.c. of the oil are mixed with 25 c.c. of 98 per cent. alcohol and 5 c.c. of silver nitrate solution (prepared by dissolving 1 gram of the nitrate in 100 c.c. of 98 per cent. alcohol). The mixture is heated to 84°. If cotton-seed oil be present, even in very small quantity only, the mixture will become coloured, and take a tint more or less deep according to the amount of cotton-seed oil present. This method depends on the property possessed by cotton-seed oil of reducing silver nitrate. It is necessary to avoid heating by a direct flame, or other oils which may be present, such as linseed oil, colza, &c., will give colorations.

J. T.

**Estimation of Fragrant Essential Oils.** By A. LEVALLOIS (*Compt. rend.*, 99, 977—980).—If an aqueous or alcoholic solution of bromine is added gradually to an aqueous or alcoholic solution of an essential oil (for example, rose, geranium, neroli, rosewood, bergamot, lemon, orange, lavender, marjoram, cummin, eucalyptus), the colour of the bromine solution is discharged up to a certain point, beyond which any further addition of bromine produces a permanent coloration. The end of the reaction is also distinctly marked by the disappearance of the odour of the essential oil, and, if the oil and bromine are in aqueous solution, by the sudden appearance of a whitish resinous precipitate. The amount of bromine required is always proportional to the amount of essential oil present, but a correction must be made for the quantity of bromine solution (0·2—0·3) necessary to impart a distinct coloration to the quantity of liquid employed (25—30 c.c.).

When an aqueous solution of an essential oil is distilled in a flask connected with a Liebig condenser, the whole of the oil comes over with the first 20—50 c.c. of the distillate, according to the amount of oil present.

The author's method consists in concentrating the essential oil by distillation, and titrating the first portion of the distillate with a

solution of bromine, standardised by means of a standard solution of the particular essential oil.

C. H. B.

**Assay of Commercial Quinine Sulphate.** By J. E. DE VRIJ (*Jour. Pharm.* [5], 9, 454—456).—The author has examined numerous samples of commercial quinine sulphate by the method proposed by Oudemans (*Annalen*, 182, 33). A boiling solution of commercial sulphate (5 grams in 200 c.c. water) is treated with a concentrated boiling solution of Rochelle salt (5 grams). The crystals of quinine tartrate formed on cooling are collected in a filter, washed with a little water, and air dried. Cinchonidine tartrate does not separate out under these conditions. The results thus obtained, combined with optical examination as detailed by Oudemans, show that the amount of cinchonidine sulphate occurring in commercial quinine sulphate varies from 5.47 to 18.46 per cent.

J. T.

**New Reactions for Codeïne and Æsculin.** By L. RABY (*Jour. Pharm.* [5], 9, 402—403).—To the codeine placed in a watch-glass add two drops of ordinary sodium hypochlorite, dilute, and then four drops of concentrated sulphuric acid; after mixing with a glass rod, a superb clear blue coloration is produced. Bromine-water, in place of hypochlorite, gives no coloration. Bromine-water employed alone causes a turbidity at the point of contact with the alkaloïd; by agitation, the liquid becomes clear and perfectly colourless, but after a few seconds a violet coloration appears, faint but perfectly distinct. In experimenting with 30 of the most common alkaloïds, none of them gave a coloration that could be confounded with the one given by codeïne.

An equally beautiful coloration is produced with æsculin when somewhat differently treated. Four drops of concentrated sulphuric acid are added to the æsculin, and to the slightly coloured liquid which is formed, sodium hypochlorite is gradually added, with agitation. When sufficient of this reagent has been added, the liquid takes an intense violet coloration; this gradually and totally disappears in about an hour. No coloration is produced if the additions are made in the inverse order. Bromine-water substituted for hypochlorite gives a precipitate of the colour of dregs of wine; the reaction is much less certain than with hypochlorite.

J. T.

**Estimation of Tannin.** By P. CARLES (*Jour. Pharm.* [5], 9, 33—35).—The author finds that in estimating tannin by titration with a solution of gelatin, the solution can be made to clear quickly by the addition of 2—3 grams of barium sulphate; the clearing takes place most rapidly towards the end of the titration. To make quite sure of the finish, a little liquid is taken out, filtered, divided into two portions, and tested with gelatin and tannin solution respectively.

The weak point of the method is the instability of gelatin solution. However, after numerous experiments, the author finds that cherry-laurel water preserves the solution for months in well-closed bottles. The solution is prepared as follows:—Gelatin 2 grams, boiling water

1000 ; when all is dissolved, cool, add 150 of cherry-laurel water, make up to 1500 c.c. and filter ; 45 c.c. are equal to 0.05 gram of tannin.

J. T.

**Adulteration of Pepper.** By H. RABOURDIN (*Jour. Pharm.* [5], 9, 289—297).—This paper deals mainly with the adulteration of pepper by the addition of ground olive-stones and pepper refuse. The microscope shows the presence of these adulterants ; the author has devised a method of estimating the amount. 1 gram of the pepper, shown by the microscope to be adulterated with ground olive-stones, is boiled for an hour with 100 grams water and 1 gram sulphuric acid, water being added from time to time to replace that evaporated. The flask is best suspended by its neck on account of the bumping which takes place. The residue is cooled and thrown on to a weighed filter, washed, dried, and weighed. The presence of olive-stone powder is shown by the reddish powder which settles to the bottom of the flask on standing ; pure pepper does not give a dense reddish residue. Numerous experiments show that the following coefficients are obtained for different varieties of pure pepper. White pepper, 0.175 ; Malabar, Tellichery, and Saigon, 0.30 ; Aleppo, 0.32 ; other commercial peppers, the so-called light varieties, 0.35. On the other hand, the varieties of ground olive-stones of commerce give numbers closely approximating to 0.745. Pepper refuse, consisting largely of the epidermis, gives 0.655. Commercial peppers, guaranteed pure, of different varieties, have been found to give  $0.497 = 44$  per cent. of adulterant,  $0.50 = 45$  per cent., and so on.

Samples of known purity were mixed with different amounts of adulterant, and when examined by this method, gave results always within 2 per cent., and frequently within 1 per cent. of the truth.

J. T.

**Estimation of Nitrogen in Urine and Fæces.** By W. CAMERER (*Zeit. f. Biol.*, 20, 255—263).—Instead of the ordinary method of evaporating the urine to dryness on a water-bath with oxalic acid and gypsum, the author substitutes the following plan. A piece of thin-walled glass tubing capable of holding 6—7 c.c., and passing easily down the combustion tube, is fused at one end, to the other is fitted a solid paraffin cap, their weight noted, and then the tube is nearly filled with urine, the cap replaced, and carefully melted into the tube (by means of a lighted taper), to prevent any escape of urine, and finally weighed. The combustion is carried out in the ordinary way, the tube being placed between two long layers of soda-lime.

Applying the same principle to the fresh fæces, the author has been able to determine by comparative experiments the loss of nitrogen caused by the usual method of drying fæces at 100—105° before combustion. The mean result of several analyses shows that a loss of a little over 0.1 gram occurs for every 100 grams of fresh fæces, which is an important discrepancy, considering the normal daily elimination is between 150—200 grams.

J. P. L.



## Technical Chemistry.

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**Recovery of Sulphur from Hydrogen Sulphide.** By C. F. CLAUS (*Dingl. polyt. J.*, **254**, 355).—It has been found that on passing hydrogen sulphide mixed with a quantity of atmospheric oxygen equivalent to its hydrogen, through a layer of ferric oxide, the temperature often rises above the point suitable for the operation, and fused masses are produced. To overcome this difficulty, other substances which will effect a finer division of the ferric oxide are mixed with the latter. Alumina, magnesia, lime, baryta, their sulphates or carbonates, oxides of zinc, chromium, &c., may be used. Instead of ferric oxide, other oxides, and metallic salts capable of decomposing hydrogen sulphide at an elevated temperature may be employed. For instance, chromic oxide, chromates, the oxides of copper and manganese, manganates, &c. If a soluble salt is employed, for instance, copper sulphate, a chromate, &c., it is best to soak porous substances such as cubes of porous clay, pumice stone, or similar materials in its solution, and dry them. Before use, these substances are broken into sizes varying from a walnut to a pea, and are placed in a layer from 150 to 300 mm. deep on the perforated bottom of an iron tank lined with clay masses. Beneath the false bottom are two apertures, by one of which the hydrogen sulphide is allowed to enter, and by the other atmospheric air. The free sulphur formed in the operation escapes through an opening in the tank, and is collected in suitable chambers.

D. B.

**Purification of Sulphuric Acid.** By W. J. MENZIES (*Dingl. polyt. J.*, **254**, 400).—The author obtains sulphuric acid of the highest concentration, containing only traces of iron or arsenic, by distilling pyrites acid in the presence of a powerful oxidising agent, such as nitric acid. For this purpose ordinary chamber acid of not less than 58° B. is treated with some nitric acid, and introduced into an iron pan provided with a condenser consisting of a range of iron pipes. The pan is then heated by a flue from the fire place, so arranged that the sides of the pan only are exposed to the heat. The distillation is continued until the condensed acid has a concentration of about 60° B., when the operation is stopped and the liquid allowed to settle. The acid is then withdrawn, and will be found practically free from iron and arsenic, and 3 or 4 per cent. stronger than the ordinary 66° Baumé acid of commerce.

D. B.

**Preparation of Ammonia from Nitrogenous Minerals.** By G. BEILBY (*Dingl. polyt. J.*, **254**, 342—345).—According to a table of analyses in *Watts's Dictionary*, natural bitumens contain from 1 to 2·3 per cent. nitrogen. The oils prepared artificially by the destructive distillation of carbonaceous substances also contain considerable quantities of nitrogen. Oils obtained by the distillation of coal contain 5 to 10 per cent. of the total nitrogen originally present in the coal, and shale oils 20 to 30 per cent. In 1871, the author investigated the

distribution of the nitrogen of bituminous shales when distilled for the production of paraffin. It was found that 100 parts of the nitrogen in the original shale was divided in the products as follows:—In the ammoniacal water 17·0 per cent., in the oil as basic tar 20·4 per cent., and in the residue or coke 62·6 per cent. By subjecting the oil to distillation, free ammonia is given off, an oil being obtained which contains only a small amount of nitrogen, whilst the residue shows from 2·8 to 3·2 per cent. nitrogen. The residue from the distillation of the basic tar contains about 4 per cent. of nitrogen.

In prosecuting these researches, the author found that an increase in the yield of ammonia was effected, when the distillation was conducted very slowly, as the coal was exposed to a red heat for a longer period. The same effect was produced when steam was used for the distillation of bituminous shales, the yield of ammonia being further increased by passing steam through the red-hot residue. 100 parts of the total nitrogen originally present gave the following distribution:—In the ammoniacal water 24·2 per cent., in the oil as basic tar 20·4 per cent., and in the residue or coke 55·3 per cent. nitrogen. It was found possible, however, to obtain almost all the nitrogen of the coke as ammonia by igniting the coke in steam. Samples of coke ignited in fire-clay retorts gave the following results:—Nitrogen in the ammoniacal water 74·3 per cent., in the oil as basic tar 20·4 per cent., and in the residue 4·9 per cent. Retorts of small capacity gave unsatisfactory results, owing to the fusibility of the ash of various bituminous shales, but no difficulty has been experienced with large retorts, in which the material remains under the influence of heat and steam for a longer time and at a somewhat lower temperature.

In 1882, the author discovered that a certain proportion of air could be mixed with the steam without reducing the yield of ammonia. A certain amount of heat is thereby generated within the retort, and consequently less has to be supplied from the outside. A retort worked alternately with steam alone and with a mixture of steam and air, showed with the latter a gain of 10 per cent. of paraffin oil and 25 per cent. of solid paraffin.

The author has investigated the application of this process to the recovery of ammonia and water-gas from coal. The difficulty experienced is that the temperature necessary for carbon to act on water is at least 1100—1200°. According to Ramsay and Young, however, decomposition of ammonia begins at 500°. It is necessary therefore to reduce the chances of contact of the ammonia molecules with surfaces at the decomposing temperature; this may be effected by diluting the ammonia-gas with steam. Air may be made to take the place of a part of the steam. Retorts have been erected at the Oakbank works for the carbonisation of coal by means of steam. The coal is burned in the lower part of the retort with steam and air. When the heat is properly regulated, the tar is completely decomposed, only a small amount of pitch being deposited in the condensing pipes. The apparatus worked at Oakbank gives a yield of 40—50 kilos. ammonium sulphate per ton of dross, equal to 60—70 per cent. of the total nitrogen present. The amount of steam used varies from 1116 to

1563 kilos. per ton of coal. The composition of the water-gas differs somewhat according to the temperature and air supply. A sample showed the following composition:—

CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H.	N.
16·6	8·1	2·3	28·6	44·4

D. B.

**Working up the Mother-liquors from Schoenite in the Production of Kainite.** By VORSTER and GRÜNEBERG (*Dingl. polyt. J.*, **254**, 355).—The liquors obtained in the preparation of schoenite from kainite are evaporated to a density of about 35° B. During this operation, a mixture consisting of sodium chloride, calcium chloride, potassium magnesium sulphate, and magnesium sulphate is separated; this contains the greater part of the potassium and sulphuric acid originally present in the liquors. The potassium may be recovered from this saline mixture in the form of potassium magnesium sulphate, by treatment with hot kainite mother-liquors.

D. B.

**Chemical Reactions in the Setting of Hydraulic Mortars.** By H. LE CHATELIER (*Bull. Soc. Chim.*, **42**, 82—89).—A complete theory of the setting of mortars includes the physical and the inducing chemical phenomena. As regards the former, it has already been shown that the process of hardening results from the successive dissolution and crystallisation of the calcium hydroxide. The reactions taking place between the combinations of the lime, silica, and the oxides of aluminium and iron are here studied. The principal ingredient in hydraulic mortars is a hydrated calcium silicate of the approximate composition  $2(\text{CaO}, \text{SiO}_2) + 5\text{H}_2\text{O}$ ; this is decomposed by excess of water to form another silicate of the composition  $2\text{SiO}_2, \text{CaO} + \text{H}_2\text{O}$ , although this change is arrested by the presence in the water of 0·5 gram of lime in the litre. A larger quantity of water decomposes this acid silicate to form silica, whilst carbonic acid converts it completely into calcium carbonate and silica. The formation of the silicate in the hardening of the mortar results from a variety of causes, as by the direct combination of the lime and silica, by the decomposition in contact with water of a basic calcium silicate, and possibly by the hydration of anhydrous calcium silicate. These several chemical changes are here discussed; the first occurs in the preliminary calcination and fusion of artificial mortars, the second, or most important, reveals itself by the separation of crystalline calcium hydroxide, whilst the third, although not reproducible in the laboratory in the case of calcium silicate, has yet been effected in the corresponding barium compound.

Besides the silicates there are present in the mortars calcium aluminate and ferrate, of the composition  $\text{Al}_2\text{O}_3, 4\text{CaO}, 12\text{H}_2\text{O}$  and  $\text{Fe}_2\text{O}_3, 4\text{CaO}, 12\text{H}_2\text{O}$ , decomposed by water and carbonic anhydride, with separation of ferric oxide and alumina. Their presence is, however, most important in the preliminary fusion of the mortars, as serving to melt the lime and the silica, thus effecting their combinations by the more immediate contact.

Lately, as regards the combination of the free lime with the

carbonic anhydride, the author shows that this change is not essential to the setting of the mortar, but although limited to the superficial layers, it materially assists its preservation. V. H. V.

**Roman Alunite.** By C. SCHWARZ (*Ber.*, **17**, 2887—2888).—The author has roasted alunite at different temperatures, and extracted the product with sulphuric acid at different degrees of strength, in order to ascertain the conditions for obtaining the greatest amount of alumina and potash in solution. He recommends that the mineral be roasted at 500°, and then treated with sulphuric acid of sp. gr. 1·297 to 1·530 (comp. Guyot, *Abstr.*, 1883, 250 and 397).

A. K. M.

**The Moulding of Porcelain.** By C. LAUTH (*Bull. Soc. Chim.*, **42**, 560—567).—The ordinary process of porcelain moulding consists in pouring the thin porcelain paste into dry plaster moulds; after a time, the paste adhering to the dry porous walls of the mould becomes set and of sufficient thickness to allow of the mould being turned upside down, and emptied of all but the thin layer of comparatively dry paste adhering to the inside; this continues to dry, shrinks, and can then be easily detached. When large mouldings have to be made, special precautions must be taken; the excess of paste is allowed to run out at the bottom of the mould, and compressed air is driven in to keep the thin layer on the walls in its position; or the liquid paste is extracted by means of a vacuum. In order that the shell may detach itself with perfect evenness from the mould, Réuard first covers the inside of the mould with a piece of muslin; by this means seams and slight imperfections do not reproduce themselves in the cast.

J. K. C.

**Purification of Zinc containing Arsenic.** By L'HOTE (*Dingl. polyt. J.*, **254**, 400).—The author has examined several specimens of zinc for arsenic, and found the following quantities in 1 kilo. of the metal:—

Zinc in sheets from Vieille Montagne.....	20 to 36 mgrms.
"          "  Honfleur .....	10·5       "
"          "  the Asturien Company..	26·0       "
Zinc in blocks from Vieille Montagne.....	traces not weighable.
"          "  Silesia .....	do.

The removal of arsenic may be effected by adding to the molten zinc 1 to 1·5 per cent. of anhydrous magnesium chloride and stirring the mixture. The arsenic is thereby volatilised in the form of trichloride of arsenic, together with white vapours of zinc chloride. The mass is granulated by pouring it into water and the zinc will then be found free from arsenic. The purification of zinc containing antimony may be effected in a similar manner. D. B.

**Manganese Steel.** By F. GAUTIER (*Dingl. polyt. J.*, **254**, 499).—Steel containing from 9 to 15 per cent. of manganese is prepared by adding ferromanganese (80 per cent. Mn) to the molten metal in quantities sufficient to produce the desired effect. The mixture is then

fused and cast. For the production of steel containing 9 per cent. manganese, 11 to 12 per cent. ferromanganese and 5.5 to 6 per cent. of carbon are added, so that the finished steel contains 0.6—0.7 per cent. carbon. Manganese steel is readily fusible, and offers a considerable amount of resistance to concussion, hence it is suitable for the manufacture of projectiles and the construction of bulwarks. Axes have been cast from this steel, with which it was possible to split iron 15 to 20 mm. in thickness without previously hardening the castings.

D. B.

**Preparation of Malleable Nickel and Cobalt.** (*Dingl. polyt. J.*, **254**, 315).—According to the "Berndorf Metal Works," fused nickel or cobalt absorbs carbon and oxygen simultaneously, and loses the greater part of the latter on cooling, so that a porous metallic mass remains, which, in consequence of the presence of varying quantities of carbon, cannot be welded. To overcome this difficulty, it is proposed to reduce pieces of pure oxide of cobalt or nickel at a moderate temperature, and to saturate the porous cubes thus obtained with a 4 per cent. solution of a manganate or permanganate of the alkali metals. The cubes are then dried and fused. The manganates or permanganates are said to suppress the injurious effect of the carbon absorbed by the castings. The oxygen may be removed by the addition of a small amount of aluminium, calcium, or an alloy of calcium with zinc and wood charcoal, to the fused metal. D. B.

**Weiller's Silicon Bronze.** By X. MÜLLER (*Dingl. polyt. J.*, **254**, 492—495).—The oxides contained in the mass of a metal or an alloy tend to impart a want of uniformity to the mass, and may deteriorate its most essential properties. Weiller's experiments in this direction have shown that the presence of minute quantities of oxides in alloys occasions a reduction in the strength and conductivity of electric wires prepared from such alloys. He proposes to remove the oxides produced during the process of fusion by means of silicon, which is added to the molten mass in the form of potassium fluosilicate. This is decomposed by sodium, the silicon which is liberated effecting the reduction of the oxides. The fluorides of potassium and sodium, together with the silica, float on the surface of the molten mass and form an excellent slag, which takes up the greater part of the unabsorbed silicon. Only small quantities of the latter are retained by the bronze. D. B.

**Formation of Patina.** By E. STEINER (*Dingl. polyt. J.*, **254**, 353).—An important element in the production of patina is the preservation of the skin of the castings. Bronzes of recent origin are defective, inasmuch as the moulds used for casting them are too porous, and have too many seams; the best results are obtained when the finest moulding sand is employed. The formation of the patina begins with the commencement of the cooling of the fused metal, and can be distinguished microscopically. It depends on the infusibility of the alloy, hence silver or similar metals are often added.

D. B.

**Manufacture of Asphalt.** By E. DIETRICH (*Dingl. polyt. J.*, 254, 354).—The author prepares a raw material suitable for asphalt paving by adding pure bitumen, *Trinidad épuré*, Goudron, or hard bitumen, to ordinary limestone or asphalt stone during the process of disintegration. On heating the mixture in drums, the bitumen is absorbed by the limestone granules, any light oils which may be present in the asphalt employed being simultaneously volatilised.

D. B.

**Process for Solidifying Mineral Oils.** By L. ROTH (*Dingl. polyt. J.*, 254, 398).—The author converts mineral oils into a solid form by dissolving a fatty acid therein, then adding a small amount of sulphuric or hydrochloric acid, and mixing with water containing about 2 per cent. of alkali. By treating crude petroleum in a similar manner, three layers are said to be obtained, the lowest containing the mechanical impurities, the middle layer the heavy hydrocarbons, such as paraffins, &c., and the upper layer the light hydrocarbons which are worked up for lighting oils. The author claims as novelty the separation of the light and heavy hydrocarbons from crude petroleum by this method, which is said to take the place of fractional distillation.

D. B.

**Substance employed to Colour Wines.** By JAY (*Bull. Soc. Chim.*, 42, 167—168).—A substance known as *Tintura por los vinos* is largely used in the district of Huesca for colouring Spanish wines. It contains two coal-tar derivatives, one of which is that form of Biebrich red which is turned blue by sulphuric acid, whilst the other, which exists in smaller proportion, closely resembles the colouring matter known as *cerise*. The composition of the *Tintura* is:—Organic matter, mainly Biebrich red, 66·4; sodium sulphate, anhydrous, 26·10; arsenious oxide, 1·62; loss, iron, lime, &c., 5·88 = 100. The presence of arsenic is of special importance.

C. H. B.

**Composition of Butter from Cow's, Goat's, and Ewe's Milk.** By E. SCHMITT (*Ann. Agronomiques*, 10, 496—500). The author gives the composition of four samples of genuine butter of known origin, according to analyses and calculations made in the manner finally recommended by him:—

	Butter from			
	Cow's milk (Isigny).	Cow's milk (Flanders).	Goat's milk.	Ewe's milk.
1. Fusing point (Rudorf's method)	36·5°	36·5°	33·5°	37·5°
2. Proximate analysis (Grandeau's method)—				
Fat .....	86·25	86·50	75·0	—
Water .....	9·80	10·54	22·40	—
Casein .....	2·225	1·42	1·75	—
Ash .....	0·10	0·85	0·18	—
Not determined, and loss ....	1·625	0·69	0·67	—
			y 2	

	Butter from			
	Cow's milk (Isigny).	Cow's milk (Flanders).	Goat's milk.	Ewe's milk.
3. Fixed and insoluble fatty acids (Hegner and Angell's method).	88.57	89.15	84.40	85.25
4. Fusing point of fixed fatty acids	39.8°	40°	38.8°	40.5°
5. Volatile and soluble fatty acids, reckoned as butyric acid (Le- chartier's process, modified) ..	4.452	4.45	4.505	4.77
6. Composition of the fat (calcu- lated)—				
Butyrin.....	5	5	5.50	6
Olein .....	60	60	64.0	58
Margarin .....	35	35	30.50	36

The composition of the fat is calculated from the analyses with the aid of the table given by Chevreul (*Agenda du chimiste*, 1883, 256).

J. M. H. M.

**Separation of Soap from the Leys by Centrifugal Means.** (*Dingl. polyt. J.*, **254**, 399).—According to the *Fabrik chemischer Producte* in Berlin, the soap separated by salt instead of being cooled thoroughly, so as to effect the separation of the soap from the leys, is subjected whilst hot to centrifugal force in a drum. The soap separated in this way is said to contain no leys, only traces of salt, and less water, and is denser and perfectly neutral.

D. B.

**Preparation of a Yellow Rosaniline Dye.** By F. MACHENHAUER (*Dingl. polyt. J.*, **254**, 272).—On treating a hot solution of 1 part azuline in 20 parts glacial acetic acid, with 3 parts nitric acid or a corresponding amount of nitrous acid, nitrate, or nitrite, the blue is converted into a yellow colour. A similar result is obtained on nitrating an aqueous solution of the sulphonic acid of azuline. For this purpose, 20 parts of the sulphonic acid, obtained by treating 1 part azuline with 5 parts of sulphuric acid are dissolved in 20 parts of water and treated with 2 parts nitric acid at 100°.

D. B.

**Preparation of New Colouring Matters.** (*Dingl. polyt. J.*, **254**, 389—396).—A process for preparing violet, blue, and green dye-stuffs of the rosaniline group has been patented by the *Badische Anilin und Soda Fabrik*, which is essentially an extension of Caro and Graebe's synthesis of aurin from phenol and hydroxy-derivatives of benzophenone in the presence of phosphorus trichloride (*Abstr.*, 1879, 60). The following derivatives of benzophenone are used:—Tetramethyldiamidobenzophenone, tetrethyldiamidobenzophenone, dimethylamidobenzophenone, and the diethyl-derivative of paramido-

benzophenone. Aromatic amines:—Diphenylamine, phenyl- $\alpha$ -naphthylamine,  $\alpha$ -dinaphthylamine, and the tertiary alkyl-derivatives of aniline, orthotoluidine,  $\alpha$ -naphthylamine, orthanisidine, metaphenylenediamine, and quinoline.

The action of the carbonyl group of amidobenzophenone, like that of the corresponding hydroxy-ketones on hydrocarbon residues, does not take place directly, but is effected through the medium of phosphorus trichloride or phosphorus oxychloride. Carbonyl chloride, phosphorus pentachloride, the bromine and iodine compounds of phosphorus, phosphorus oxybromide, and phosphorus sulphochloride act in a similar manner. The condensation takes place also in the presence of aluminium chloride. The dyes obtained by the condensation of the tetra-alkyl diamidobenzophenones with the above-named aromatic amines give violet or blue colours resembling methyl-violet, whilst the corresponding colouring matters of the di-alkyl amidobenzophenones are green and resemble malachite-green in properties. The green dye-stuffs from quinoline and the alkyl-derivatives of diamidobenzophenone belong to the latter category.

The preparation of a new group of basic dyes called auramines is likewise described by the Baden aniline works. The simplest members of this group are yellow dyes formed from tetra-alkyl diamidobenzophenones by the action of ammonia on the methane residue. When these dyes are heated with aniline, its homologues, or naphthylamine, &c., phenyl, tolyl, naphthyl auramines, &c., are obtained, which give redder or browner colours.

Ewer and Pick prepare sulphuretted dyes by heating equal molecular proportions of sulphur and paranitraniline, paranitrethylaniline, or paranitrodimethylaniline, thus forming the corresponding thio-compound, which is converted into thiotetramine by reduction. The latter is then subjected to oxidation, and accordingly as it has been formed from a primary, secondary, or tertiary paranitramine, violet, blue, or greenish-blue colouring matters are produced. The derivatives of orthotoluidine, orthamidoanisole, and orthamidophenetol may be used in the place of aniline. By introducing alkyl-groups into the primary or secondary amido-group of thioparanitramines, the corresponding secondary and tertiary amines are obtained.

For the production of azo-colours from tetrazo-diphenyl, Böttger mixes aqueous solutions of tetrazodiphenyl salts with salts of  $\alpha$ - or  $\beta$ -naphthylamine, or  $\alpha$ - or  $\beta$ -naphthylamine sulphonic acids. The colouring matters obtained in this way impart a permanent red colour to wool and cotton, in the case of the latter, without the use of mordants.

D. B.

**Benzaldehyde-green.** (*Dingl. polyt. J.*, **254**, 316.)—According to *Dittler and Co.* in Griesheim a bluish-green dye is obtained by dissolving a salt of benzaldehyde-green in water, acidifying with acetic acid and adding chloride of lime. 25 kilos. of tetramethyldiamidotriphenylcarbinol oxalate are dissolved in 1000 litres cold water, acidified with 50 kilos. acetic acid, and treated with 7 kilos. chloride of lime made into a sludge with water. The mixture is allowed to stand for half an hour and filtered. The solution is



neutralised with ammonia, filtered, the colour base dried, dissolved in hydrochloric acid, and treated with sodium chloride to precipitate the green dye. It is also proposed to dissolve 53 kilos. of the oxalate green in 2000 litres of water, acidify with 100 kilos. hydrochloric acid, treat with an alkaline solution containing 18 kilos. bromine, and precipitate with ammonia. The base produced has a bronze colour and gives up the dye on the addition of an acid. The salts of tetrethyldiamidotriphenyl carbinol give similar colouring matters.

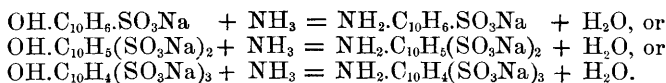
D. B.

**Preparation of Dyes from Alizarin and other Anthracene Colouring Matters suitable for Calico Printing.** (*Dingl. polyt. J.*, **254**, 224—226).—In printing cotton goods with alizarin, nitro-alizarin, or alizarin-blue, Gagenburg of Rydboholm (Sweden) and Leverkus of Cologne recommend the use of preparations which render the mordanting of the fabric needless. For this purpose, commercial alizarin, nitroalizarin, or alizarin-blue (10—20 per cent. paste) is pressed by hydraulic pressure into a mass containing from 40 to 50 per cent. solid matter, and subsequently dried at 130—140°. The dry powder is then ground in a colour mill with 4 parts of oil, and the mixture passed through Matter's straining machine (*ibid.*, **252**, 111). A colour for red is then prepared in the following manner:—Thickening material: 6 kilos. starch, 6 kilos. flour, 60 litres water, and 10 litres acetic acid of 8°. Colour: 2750 grams thickening agent, 470 "fatty alizarin" (20 per cent. paste), 30 stannous chloride (24°), 548 aluminium acetate (10°), and 280 calcium acetate. Instead of aluminium acetate, thiocyanates may be used. The other alizarin-dyes are prepared in a similar manner.

It is stated that the proposal to treat alizarin with fatty substances before use in dyeing is not new. About 10 years ago Forster, in Augsburg, suggested that the alizarin should be dissolved in an alkaline saline solution of the fatty acid and precipitated by means of an acid, an intimate mixture of dye with fatty acid being obtained which gave good results in dyeing.

D. B.

**Preparation of Naphthylamine Compounds.** By L. LANDSHOFF (*Dingl. polyt. J.*, **254**, 232).—In order to convert the hydroxyl-group of naphthyl compounds of the  $\beta$ -series into the amido-group, it is necessary to work with a pressure of from 30 to 40 atmospheres. To avoid using this pressure, the author recommends to heat the alkali salt of  $\beta$ -naphtholsulphonic acid for 12 hours at 200—250°, and pass a slow current of gaseous ammonia through the solution. The reactions



take place.

D. B.

**Preparation of Naphthol-green.** (*Dingl. polyt. J.* **254**, 184.)—According to the Frankfort Aniline Works, Gans and Co., 27.5 kilos. sodium nitroso- $\beta$ -naphtholmonosulphonate are dissolved in

100 litres of water and treated with 20 litres of a solution containing 5 kilos. of ferric chloride. The excess of iron is then removed by the addition of an alkali, and the filtrate evaporated to dryness. The resulting green dye is purified by recrystallisation from weak alcohol. Instead of using Schaeffer's monosulphonic acid, all other naphtholsulphonic acids, excepting the  $\beta$ -naphthol- $\alpha$ -monosulphonic acid and the  $\beta$ -naphthol- $\gamma$ -disulphonic acid, may be employed. By replacing the ferric chloride by equivalent quantities of a salt of cobalt or nickel, brown or yellow colouring matters are produced.

D. B.

**Turkey-red Oil.** By A. MÜLLER-JACOBS (*Dingl. polyt. J.*, **254**, 302—312).—In the *Mittheilungen des Technologischen Gewerbemuseums in Vienna*, 1884, 59, Liechti and Suida give a reply to the author's theories regarding the composition and mode of action of Turkey-red oil (see Abstr., 1884, 946). The present communication deals with the author's criticism on this reply. Liechti and Suida base their theory as to the formation of the "compound soluble in water" on the evolution of large quantities of sulphurous anhydride thus:— $2C_3H_5(C_{18}H_{33}O_2)_3 + 7H_2SO_4 = C_{42}H_{76}O_{12}S + 4C_{18}H_{34}O_3 + 4H_2O + 6SO_2$ , although they arrive at a different result in a more recent equation,  $2C_3H_5(C_{18}H_{33}O_2)_3 + 7H_2SO_4 + 8H_2O = C_{42}H_{82}O_{12}S + 4C_{18}H_{36}O_3 + 6H_2SO_4$ . The evolution of sulphurous anhydride indicates that the process of saponification has not been conducted in a proper manner, in which case only would deoxidation of the sulphuric acid be effected. The same applies to the treatment of oleic acid with sulphuric acid. This reaction is also explained differently by Liechti and Suida in their reply, and more in accordance with the views of the author; but although they appear to confirm the opinion that the best yield of soluble substance is obtained when the action of the sulphuric acid is not carried too far, they decline to accept Müller-Jacob's process, and stipulate that the sulphuric acid should remain in contact with the oil for twelve hours as before. They doubt, moreover, the presence of unaltered oil (triglyceride) in the products of the reaction. The presence of this compound can, however, be established by dissolving the products of the reaction in 10 to 12 times the volume of alcohol, when the mixture becomes turbid and gradually deposits a precipitate of the triglyceride.

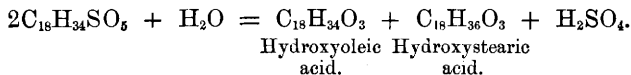
The author, in the second part of the paper, criticises the chemical questions raised by Liechti and Suida.

D. B.

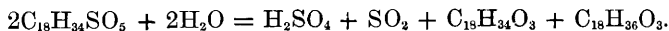
**Müller-Jacob's Investigations on Turkey-red Oil.** By H. SCHMID (*Dingl. polyt. J.*, **254**, 346—350).—The author is of opinion that the researches by Liechti and Suida (*ibid.*, 1883, **250**, 543) and A. Müller-Jacobs (Abstr., 1884, 946, and preceding Abstract) on Turkey-red oil do not fully solve the problem of the constitution and mode of action of the above-mentioned compound. According to Liechti and Suida, the conversion of olive oil depends on the formation of soluble glyceryl sulphate hydroxyoleate, the sulphuric acid acting both as oxidising and saponifying agent. An important fact which these investigators failed to observe is the production of

hydroxystearic acid,  $C_{18}H_{36}O_3$ , discovered by Müller-Jacobs. It has recently been demonstrated by Liechti and Suida that the decomposition products of their compound contain, in addition to hydroxyoleic acid, large quantities of hydroxystearic acid. The latter, however, differs from oleic acid by containing more of the elements of water,  $C_{18}H_{34}O_2 + H_2O = C_{18}H_{36}O_3$ , so that the action of sulphuric acid on oil must now be regarded in a different manner from that originally indicated by Liechti and Suida. The oxidising action of sulphuric acid, and consequent evolution of sulphurous anhydride, therefore depends only on the amount of hydroxyoleic acid formed besides hydroxystearic acid, as the latter is produced by the addition of water to the former. The author submits that this correction, that is restriction or complete suppression of the oxidising influence of sulphuric acid, does not invalidate the theory upheld by Liechti and Suida, as it is easy to imagine that by the action of sulphuric acid an oil, glyceryl sulphate hydroxystearate, accompanied or not by glyceryl sulphate hydroxyoleate, is formed.

According to Müller-Jacobs, Turkey-red oil is a mixed solution of sulpholeic acid,  $C_{18}H_{33}(SO_3H)O_2$  (soluble in water) hydroxyoleic and hydroxystearic acids (soluble in alcohol), and unaltered triglyceride (soluble in ether). It is also stated that decomposition takes place when sulpholeic acid is boiled with water, a mixture of hydroxyoleic and hydroxystearic acids being obtained, thus:—



The incorrectness of this formula is shown by the fact that the oxidising influence of the sulphuric acid has been disregarded in the formation of these acids. The production of hydroxystearic acid by the decomposition of sulpholeic acid can be expressed by the formula  $C_{18}H_{33}(SO_3H)O_2 + 2H_2O = H_2SO_4 + C_{18}H_{36}O_3$ ; hydroxyoleic acid can, however, be formed from sulpholeic acid only by assuming that the oleic acid separated is oxidised at the expense of the sulphuric acid thus:— $C_{18}H_{33}(SO_3H)O_2 = SO_3 + C_{18}H_{34}O_3$ . Müller-Jacob's formula must therefore be altered to the following:—



The same chemist believes that Turkey-red oil contains 30 per cent. or more of unaltered glycerides, and attributes the principal action of the mordanting to the presence of this compound. The unaltered oil is said to enter the colour lake and surround it in a manner, keeping it damp and protecting it from exterior influences, thus imparting brightness, softness, and solidity to the colour, an opinion which S. Jenny has already expressed, and which Müller-Jacobs has applied to the new Turkey-red oil. The action of the latter as a mordant is due to its yielding oil to the fibre in a finely-divided form, and in the best processes the remaining substances (sulpholeates) are said to be removed by washing. Nevertheless, the author has succeeded in dyeing alizarin without Turkey-red oil, by the application of ammonium

ricinoleate, and although finely-divided triglycerides were not present the reds produced compared favourably with alizarin-red as obtained by the Turkey-red process.

D. B.

**Composition of Turkey-red Oil.** By L. LIECHTI and W. SUIDA (*Dingl. polyt. J.*, **254**, 350—352).—A brief reply to Müller-Jacob's criticism of the author's researches on the constitution of Turkey-red oil.

D. B.

**Behaviour of Different Ferric Oxide Mordants with Silk.** By L. LIECHTI and W. SUIDA (*Dingl. polyt. J.*, **254**, 437—439).—For the purpose of comparison, the following iron mordants were prepared :—(1)  $\text{Fe}_2(\text{SO}_4)_{2.5}\text{OH}$  of 30° B.; (2)  $\text{Fe}_2(\text{SO}_4)_2(\text{NO}_3)\text{OH}$  of 30.5° B.; and (3)  $\text{Fe}_2(\text{SO}_4)_2(\text{OH})_2$  of 31° B. The quantities of ferric oxide fixed to the animal fibre by dissociation were determined by steeping a weighed quantity of silk in these solutions, washing the silk, drying and incinerating it, and estimating the iron in the ash. The mordant (3) gave the best result, 12 per cent. of ferric oxide having been taken up by the silk fibre as compared with 8 per cent. absorbed from the mordant (1). This result was expected, as the compound (3) has a tendency to split up into more basic salts, all of which are too unstable to be of practical utility. It is a remarkable coincidence that the mordant (2) gives a result which is almost as favourable as that of the compound (3), giving up 11 per cent. of ferric oxide. But before arriving at a conclusion as to the practical utility of this mordant, the experiment should be repeated. Most of the iron mordants examined by the authors had the formula  $\text{Fe}_2(\text{SO}_4)_{2.5}\text{OH}$ , and sometimes contained a considerable amount of nitric acid.

Referring to the influence of ferrous oxide in iron mordants, it has been ascertained by experiment that, with an increase in the percentage of this oxide, the degree of dissociation on dilution with water diminishes. The authors have, however, found that the dissociation effected by the animal fibre is the same for ferrous and ferric oxide mordants. New trials should, therefore, be made to solve this problem before the use of mordants containing ferrous oxide is completely rejected.

D. B.

**Blasting Powder.** By A. GACON (*Dingl. polyt. J.*, **254**, 355).—1 kilo. of this powder is said to blow up 12 to 15 cubic metres of rock. It requires for ignition a temperature of 480°, and cannot be exploded by concussion, not even when hammered on an anvil. It is obtained by mixing 69 parts of potassium or sodium nitrate with 19 parts of sulphur and adding ash (?) rich in potash or soda to the mixture. It is proposed to obtain this ash by burning dead leaves. 200 grams of tannin dissolved in 8 litres of water are then added to the mixture.

D. B.

**Preparation of Weatherproof and Incombustible Paper.** By W. HERRE (*Dingl. polyt. J.*, **254**, 315).—The materials used for the manufacture of incombustible and weatherproof paper or pasteboard are treated with saline solutions, for example, a solution containing

15—18 grams zinc sulphate or chloride in 1 litre, and ground to a pulp in a rag engine. 100 kilos. of the prepared pulp are then mixed with 1 to 5 kilos. tallow soap, 1 to 5 kilos. size, and 4 to 16 kilos. alum, and made into paper or pasteboard in the usual manner. Before the final drying the treatment with zinc sulphate is repeated. To render the paper weatherproof, it is steeped in a solution of catechu.

D. B.

**Enamelling Casks.** By F. G. SPONNAGEL (*Dingl. polyt. J.*, **254**, 443).—Instead of coating the wood of casks with the enamel, the latter is allowed to form in the wood in the following manner:—The cask or vat is in the first place treated with an aqueous solution of an enamel obtained by fusing 100 parts of pure silica with 50 parts of alkali. It is then filled with a solution of aluminium acetate in water mixed with sulphurous acid in the proportion of 4 : 2 : 1. The solution acts on the enamel which has penetrated into the wood, and produces a neutral enamel of silica within the pores of the wood.

D. B.

## General and Physical Chemistry.

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**The Second Spectrum of Hydrogen.** By B. HASSELBERG (*Phil. Mag.* [5], 17, 329—352).—The author's observations tend to show that Wüllner's so-called acetylene spectrum is in reality the spectra of hydrogen and of carbonic oxide superposed. The second hydrogen spectrum has been attributed to the formation of acetylene in consequence of the presence of traces of carbon-compounds in the hydrogen tubes. The author, however, has made experiments which disprove this. With a tube filled with pure hydrogen, he observed mere traces of the second spectrum when the tube was observed transversely; but the spectrum was fully developed when the tube was viewed longitudinally. R. R.

**Spectral Lines of Metals Developed by Exploding Gases.** By G. D. LIVEING and J. DEWAR (*Phil. Mag.* [5], 18, 161—173).—The researches of Berthelot have shown that the velocity of an explosion of oxygen with hydrogen is about  $\frac{1}{108000}$  of that of light; consequently if such an explosion were advancing towards the eye, the wave-lengths of successively illuminated particles would be shortened by this fraction. In the case of the sodium lines such an effect would produce a shifting of the lines towards the more refrangible end of the spectrum of about  $\frac{1}{107}$  of the space between the two lines. Conversely, a receding explosion would produce an opposite effect.

In this paper, an account is given of the spectroscopic observations made with a Rowland grating on explosions occurring in a tube bent in the form of a U, so that images of the receding and advancing explosive wave could be obtained simultaneously. The authors were, however, unable to substantiate any displacement of the relative positions of the lithium lines, owing to their breadth and diffusiveness. In the advancing flash, however, the image of the lithium lines was reversed, that is, showed a dark line down the middle, whilst the receding flash gave as broad a bright band without such a dark line. These reversals show that in the explosive wave, the temperature of the gas does not reach its maximum at once, but that the front of the wave is cooler than its successive portions. It is further established that the breadth of the lithium lines is dependent on the quantity of lithium present. In order to further study the spectra developed by exploding gases, various metals such as iron, copper, lead, cadmium, zinc, aluminium, silver and magnesium were introduced into the tube containing explosive mixtures of oxygen with hydrogen, carbonic oxide or methane, or the hydrogen-compounds of sulphur, selenium, and antimony. A description is given of the lines characteristic of each metal brought out by the explosion; among the observations, it is noticed that metals so little volatile as iron, nickel, and cobalt develop many lines, whilst more volatile metals show fewer or none.

On the whole, it may be said that the spectra so formed are similar in character to those produced by the combustion of these metals in a jet of oxygen and coal-gas. The observations of Berthelot and Vieille have shown that the temperature of the exploding gases is about  $3000^{\circ}$ ; then at this temperature iron, nickel, and cobalt are completely vaporous, and a greater number of rays emitted lie between G and P. It is suggested that the appearance of certain lines is conditioned by certain temperatures, and that it might be possible to construct a spectroscopic scale of temperature by observation on the successive development of lines concomitant with the rise of temperature.

V. H. V.

**Spectroscopic Examination of the Vapours Evolved on Heating Iron, &c., at Atmospheric Pressure.** By J. PARRY (*Chem. News*, 50, 303—304).

**Double Refraction of Liquids.** By E. v. FLEISCHL (*Ann. Phys. Chem.* [2], 24, 127—144).—Inasmuch as circular polarisation is a phenomenon common alike to doubly refracting crystals and to certain liquids and solutions of solids, the problem presents itself whether change in direction of the light rays producible by so-called optically active liquids, is due to a difference in phase of two circular polarised rays as in the case of crystals, or to some quite independent cause. In this paper, the author examines the question whether such optically active liquids are doubly refractive, though *à priori* calculations show that the degree of double refraction corresponding with their specific rotatory power is so small that it would be impossible to estimate it by any known method. A particular apparatus was constructed for the purpose, consisting of 22 hollow glass prisms within parallel glass plates; of these prisms, 20 had a refractive angle of  $120^{\circ}$ , and two of  $60^{\circ}$ ; these were arranged alternately, so that ten of the one kind and one of the other were situated with their refracting angle in the one direction, and the remainder in the other direction. The refractive angle of the whole system was equal to  $2520^{\circ}$ . The one set of prisms was then filled with some dextrorotatory solution, the other set with a lævorotatory. If then this liquid system were doubly refractive, a homogeneous ray of light should be decomposed into the ordinary and extraordinary ray. This was found to be the case, for on projecting a spot of light through this combination of prisms containing solutions of dextrose and levulose of equal and opposite rotatory power, there was observed not one but two images, side by side. A similar result was obtained with a dextrorotatory orange oil and a lævorotatory terpene. From these observations, it follows (i) that there are doubly refracting liquids, and that the ordinary and extraordinary rays undergo circular polarisation in opposite directions; (ii) that from the unequal velocity of both rays in the liquid there is produced a difference of phase proportional to the path of liquid traversed; this is the cause of the circular polarisation of the liquid. Such doubly refracting liquids have no optical axis, but the wave-surfaces of light in these liquids consist of two concentric spherical surfaces.

V. H. V.

**Amount of Atmospheric Absorption.** By S. P. LANGLEY (*Phil. Mag.* [5], 18, 289—307).—Numerous observations made under different conditions and in different localities have given for the absorption, whether of heat or of light from the sun, a value of about 20 per cent. These values have been based on two assumptions, namely, (i) that the emanating rays are homogeneous in kind, and (ii) that the absorption by the successive strata of the terrestrial atmosphere is homogeneous in degree. But by laboratory experiments Melloni has demonstrated that like proportions are not absorbed by like strata; hence it follows that the coefficient of transmission is truly constant only in the case of the absolute homogeneous ray, which can but approximately be discerned, much less discriminated, by the most delicate instruments. It is here shown by mathematical reasoning that the coefficient of transmission is (i) never a constant; (ii) always too large; (iii) increases as one approaches the horizon. But apart from mathematical considerations, the photographic spectrum near the D line, taken at 3.30 P.M., shows many more telluric lines than a spectrum taken at noon; this indicates a very small coefficient of transmission. Further, many of the telluric lines appear at great altitudes even in the clearest atmosphere. It would thus appear that there is a certain selective absorption of solar rays, and that practically between telluric lines and the general absorption there is every coefficient of transmission from unity to zero. The author believes that the actual mean absorption of sun and starlight at the sea level is probably over 40 per cent. at its minimum; and that fine dust particles, both near the surface and at a great altitude, play a more important part in the absorption, both general and selective, than has heretofore been supposed. By a complete solution of this complex question, the phenomena of meteorology would become predictable.

V. H. V.

**Method of Measuring the Chemical Effect of Radiation.** By L. OLIVIER (*Compt. rend.*, 100, 178—181).—In order to time photographic exposures, the author employs a radiometer which is provided with screens so arranged that light is only allowed to fall on the instrument during the time that the photographic plate is being exposed. The number of revolutions made by the radiometer during an exposure sufficient to give a good negative is determined once for all, and each subsequent exposure is continued until the radiometer has made the same number of revolutions. In cloudy weather the motion of the radiometer is slower, and the exposure is proportionally longer; in bright weather the motion is quicker and the exposure is proportionally shorter; but in every case the *quantity of light* which falls on the photographic plate remains the same.

The radiometer may be used in a similar manner to determine the relative sensitiveness of different plates, or the effect of different exposures on the same plate.

*Note by Abstractor.*—This method was suggested several years ago by Crookes in one of his earlier papers on the radiometer (see *Chem. News*, 51, 75).

C. H. B.



**A Diffusion Photometer.** By A. CROVA (*Compt. rend.*, **99**, 1115—1118).—This photometer is designed for measuring luminous sources of high intensity, and is based on the principle that when a translucent screen is placed in a uniformly illuminated field in a direction normal to the incident rays, each point of the screen may be regarded as a luminous source and transmits light, the intensity of which depends on the nature of the translucent material, in accordance with a law which also varies with the material, but in every case the rays diffused in a direction closely approaching the normal are equal in intensity. If there is placed behind the diffuser an opaque screen with an opening, the size of which can be varied at will, the intensity of the light normally emitted by this opening is proportional to the intensity of the luminous field in which the diffuser is placed, to a coefficient which depends on the nature of the translucent substance, and to the area of the opening, and varies inversely with the square of the distance. The author employs a Foucault's photometer, one-half of the screen being illuminated by a standard light of one Carcel lamp placed at the end of a blackened tube 1 metre in length, whilst the other half is illuminated by the light to be examined. The latter passes down a tube which is movable on a graduated circle fixed at right angles to the axis of the first tube. At the further end of this tube there is a rectangular opening, the breadth of which remains constant, whilst the length can be varied by means of a micrometer screw. This opening is placed against the diffuser, and the size of the opening is altered until the two halves of the screen of the photometer are equally illuminated. For intensities up to 400 Carcels the diffuser is made of ground glass, whilst for higher intensities opal glass is used. Formulæ for calculation are given in the paper.

C. H. B.

**The Pupil Photometer.** By J. GORHAM (*Proc. Roy. Soc.*, **37**, 425—426).

**Sunshine Recorder.** By H. MCLEOD (*Phil. Mag.* [5], **18**, 141—142).—In this paper a preliminary account is given of a sunshine recorder, in which the light, not the heat, of the sun is the agent in the production of chemical change. The apparatus consists of a camera whose axis is parallel to the polar axis of the earth, the lens pointing northward; opposite the lens is a silvered sphere. The solar rays are reflected from the latter through the camera lens on sensitive ("ferroprussiate") paper.

By the earth's motion the image is carried round in a circular arc, tracing a curve on the paper; a time scale is made by drawing from the centre of the circular band radial lines enclosing angles of 15°, each division representing one hour of time. The paper is sufficiently sensitive to register short gleams of sunshine. When the sun is shining through light clouds, a blurred impression is produced of a much less intense blue colour than that obtained by direct sunlight.

V. H. V.

*Note.*—For further details and drawings of the apparatus, see *Nature*, **31**, 319. More than six months' experience of its working has confirmed the usefulness of the results obtained by it.—A. J. G.

**New Standard of Illumination.** By W. H. PREECE (*Proc. Roy. Soc.*, **36**, 270—275).—After alluding to the unsatisfactory methods in vogue for measuring the intensity of illumination, the author suggests as a standard the *space illuminated* by a standard candle at 12·7 inches distant. For a comparison of the relative illumination of surfaces, use is made of a Swan's incandescent lamp, giving a light of  $2\frac{1}{2}$  candles with a current of 5 volts, enclosed within a box with blackened walls, over the end of which is stretched a diaphragm of paper; the latter has a grease spot at its centre. At about 12 inches from the tube is a screen of paper as a reflecting surface. The current is supplied from a secondary battery. From experiments detailed in the paper, it appears that the illuminating power of the glow lamp increases in the ratio of the sixth power of the current: hence a determination of its strength gives the necessary equivalent for ascertaining the degree of illumination. Though there are certain difficulties arising from alteration of the glass envelope of the lamp, deterioration of the carbon fibres, and failure of vacuum, yet the light emitted from the passage of a given current is more easily reproducible and probably more uniform than any other artificial standard.

V. H. V.

**Disturbing Phenomenon observed in Polarising Operations.** By SCHMIDT and HÄNSCH (*Dingl. polyt. J.*, **255**, 119).—In making observations with polarising apparatus, it is occasionally found that a filled tube, when placed in the polarimeter, does not always give the same reading when turned round the axis; this difference is observed even on filling the tube with distilled water. The causes of these disturbing influences are said to be—(1) want of uniformity of the solution; (2) dirt in the tubes; (3) imperfect parallelism of the plane of the glasses; and (4) non-parallel edging of the observation tubes.

D. B.

**Relation between the Electromotive Force of a Daniell's Cell and the Strength of the Zinc Sulphate Solution.** By H. S. CARHART (*Amer. J. Sci.* [3], **28**, 374—377).—The investigation described was undertaken with a view to ascertain to what extent the variation in the strength of the zinc sulphate solution affected the electromotive force. The method employed was essentially Poggen-dorff's compensation method. The table (p. 322) exhibits the results.

The values of the electromotive force, given in the seventh column in arbitrary units, were reduced to volts in the following manner:—The ratio of the Siemens unit to the legal ohm (this vol., p. 2) is 50 : 53, and according to Lord Rayleigh, a current of one ampère deposits 67·08 mgrms. of silver per minute. Then if C, R, and E represent current strength, resistance, and electromotive force in ampères, ohms, and volts, and  $e$  the electromotive force in the arbitrary unit of the table, we have the following equation:—

$$(R_{\frac{53}{50}})(C \times 67\cdot08) = e.$$

$$\text{whence } RC = \frac{e}{\frac{53}{50} \times 67\cdot08} = \frac{e}{71\cdot105} = E.$$

Per cent. of ZnSO <sub>4</sub> .	Temp- erature of rheo- stat.	Resistance in Siemens units.	Silver deposited in one minute. mgrms.	Product of resist- ance and silver.	Cor- rected for tem- perature of rheo- stat.	Mean value of product.	E.M.F. in volts.
0	20·0°	11	6·727	73·997	73·997	73·997	—
1	18·8	11	7·277	80·037	80·000	80·000	1·125
3	18·0	11	7·339	80·729	80·664	80·584	1·133
	19·5	12	6·710	80·520	80·504		
5	17·8	11	7·423	81·653	81·581	81·216	1·142
	17·3	11	7·358	80·938	80·851		
7·5	17·3	11	7·239	79·632	79·546	79·620	1·120
	18·3	11	7·250	79·750	79·694		
10	17·0	11	7·224	79·464	79·369	79·490	1·118
	19·3	11	7·239	79·634	79·612		
15	20·0	11	7·219	79·409	79·409	79·305	1·115
	18·3	11	7·205	79·255	79·201		
20	17·3	11	7·170	78·870	78·785	79·008	1·111
	17·5	11	7·210	79·310	79·231		
25	16·3	11	7·199	79·189	79·072	78·997	1·111
	16·6	11	7·184	79·030	78·923		

It is only necessary to divide the quantities in column 7 by 71·105 to reduce them to volts. The method employed is fully sustained by the results obtained with a Latimer Clark standard cell. The mean of all the values in the last column of the table is 1·122, which is the value obtained by Sir W. Thomson by the electrostatic method, if the velocity expressing the ratio between the electrostatic and electro-magnetic units be taken as  $3 \times 10^{10}$ .

From the results of the investigation, it appears that the variation in the concentration of the zinc sulphate solution is sufficient to account for the discrepancy between the results obtained by different experimenters in measuring the electromotive force of a Daniell cell. It therefore seems desirable that a standard Daniell cell should be so constructed as to admit of employing a zinc solution of known concentration.

B. H. B.

**Experimental Researches on the Electric Discharge with the Chloride of Silver Battery.** By W. DE LA RUE and H. W. MÜLLER (*Proc. Roy. Soc.*, 36, 151—157, and 206—207.)

**Electric Conductivity of Impure Mercury and Methods of Purification.** By C. MICHAELIS (*Chem. Centr.*, 1884, 482—484).—The metallic impurities of mercury are divided by the author into three groups, according to their action and the mode of separating them. The first group contains magnesium, potassium, and sodium; these may be completely removed by agitation with sulphuric acid. The second group contains zinc, lead, cadmium, and bismuth, which are best separated by boiling the mercury with concentrated sulphuric acid containing a few drops of nitric acid, and subsequently

treating it with dilute nitric acid. The metals of the third group are gold, silver, and copper, the last of which may be separated in the same way as the metals of the second group.

An excellent way of purifying mercury is to submit it to surface distillation in a vacuum. A. K. M.

**Electric Conductivity and other Properties of the Copper-Antimony Alloys.** By G. KAMENSKY (*Phil. Mag.* [5], 17, 270—275).—The paper gives determinations of the electric conductivities and of the specific gravities of a graduated series of alloys of copper and antimony. A maximum of conductivity was found in the alloy corresponding with the formula  $\text{SbCu}_2$ ; from this point, the curve falls very rapidly with increase of copper until it reaches  $\text{SbCu}_4$ , whence it again rises very rapidly as pure copper is approached. The specific gravities rise evenly from antimony to the alloy  $\text{Cu}_4\text{Sb}$  (sp. gr. = 8.871), and then diminish to copper. R. R.

**Electric Conductivity of Water.** By F. KOHLRAUSCH (*Phil. Mag.* [5], 18, 542—544).—The question of the conductivity of water cannot be considered to be settled, inasmuch as there are difficulties in purifying it from dissolved gases, and from solids derived from the vessels used in its distillation. The water used in the experiments described in this paper was distilled at a temperature of 30—45° under a pressure of 0.001 mm., and quickly condensed in the resistance apparatus. Observations were made at once, inasmuch as it was found that the conductivity increased with the time. The mean of eight observations gave a value of about  $30 \cdot 10^{-12}$  ohms, or practically about 72 billionths of that of mercury, or, to put the statement in another form, a thread of water 1 mm. in length has the same resistance as a thread of mercury of the same thickness encircling the earth. Water may thus be considered to be practically a non-conductor of voltaic electricity. The value obtained in these experiments is almost one-third of that found in previous researches; the water was thus presumably three times as pure. V. H. V.

**Electric Conductivity of Acids.** By W. OSTWALD (*J. pr. Chem.* [2], 30, 225—237).—In a former paper (this vol., p. 3) the author has shown that a direct ratio exists between the rapidity with which certain acids take part in a reaction, and the rate at which they conduct electricity. This latter property depends greatly on the state of dilution of the acid, as the appended table shows. The numbers in column I represent the electrical conductivities of the acids in normal solutions, hydrochloric acid being taken as 100; those under columns II, III, and IV, give the conductivities for normal solutions diluted with water, 10, 100, and 1000 times respectively.

The weaker monobasic acids show a rapid increase in their electrical conductivities with increasing dilution, and apparently all converge towards the same limit, something above 100, which the stronger acids reach at an early stage. The bibasic acids, with the exception of sulphuric acid, appear to tend towards a maximum conductivity of about 52, or half the number attained by the monobasic acids, whilst

	I.	II.	III.	IV.
Hydrochloric .....	100·0	118·0	123·8	112·2
Hydrobromic .....	101·4	119·8	125·9	112·5
Nitric .....	99·4	116·7	122·5	107·4
Ethylsulphonic .....	80·3	106·8	113·5	101·8
Ethylsulphuric .....	88·6	108·5	116·6	111·6
Isethionic .....	75·3	103·8	110·2	101·7
Phenylsulphonic .....	73·6	104·8	111·3	97·2
Formic .....	1·718	5·31	15·75	42·7
Acetic .....	0·436	1·557	4·96	14·48
Butyric .....	0·333	1·404	4·45	12·90
Isobutyric .....	0·329	1·403	4·41	12·65
Monochloracetic .....	5·06	15·26	38·9	78·2
Dichloracetic .....	24·75	64·2	79·6	103·0
Trichloracetic .....	61·1	100·3	110·2	104·4
Glycollic .....	1·390	4·65	13·90	37·1
Methylglycollic .....	1·787	6·61	19·19	47·7
Ethylglycollic .....	—	5·46	16·49	43·9
Lactic .....	1·085	4·25	13·07	35·4
$\beta$ -Hydroxypropionic .....	0·650	2·31	6·79	19·52
Glyceric .....	1·556	5·50	16·27	42·6
Pyroracemic .....	6·01	19·26	46·1	76·4
Hydroxyisobutyric .....	1·316	4·21	11·80	32·5
Sulphuric .....	65·0	77·2	102·7	113·4
Oxalic .....	19·50	38·7	53·0	52·8
Malonic .....	3·16	9·52	24·35	43·9
Succinic .....	0·695	2·061	6·16	16·91
Malic .....	1·401	4·79	13·88	33·2
Tartaric .....	2·370	6·89	20·90	45·5
Diglycollic .....	2·621	7·95	21·16	46·1
Pyrotartaric .....	1·109	3·31	8·26	20·22
Citric .....	1·728	5·49	14·32	28·82
Phosphoric .....	7·16	15·39	28·40	31·4
Arsenic .....	5·32	12·38	25·49	30·8

the limit reached by the tribasic acids is a third, or about 35. In other words, the conductivities of the three kinds of acids are the same when compared according to their molecular weights. In very dilute solutions, therefore, during electrolysis, only one of the replaceable hydrogen-atoms in each molecule is influenced by the current.

J. K. C.

**Some New Phenomena of Electrolysis.** By G. GORE (*Proc. Roy. Soc.*, **37**, 24).

**Unequal Electric Conduction Resistance at Cathodes.** By G. GORE (*Proc. Roy. Soc.*, **37**, 35—36).

**Relation of Chemical Corrosion to Voltaic Current.** By G. GORE (*Proc. Roy. Soc.*, **36**, 331—341).—The object of the experiments described in this paper was to ascertain the amounts of voltaic current produced by the chemical corrosion of known weights of various metals in different liquids. The method employed was based upon a comparison of the loss of weight of two similar plates immersed in the same liquid contained in two glass vessels. One of the pieces was

employed as the positive pole of a battery, the negative pole being a sheet of platinum. The current from the cell decomposed a solution of silver cyanide. The results obtained with different metals and liquids are given in a long series of tables. The amount of corrosion of the positive plate is in nearly all cases greater than that of the comparison plate, and the proportion of gas to corrosion was frequently less with the former than with the latter. A marked exception to this rule was copper in nitric acid. The proportion of corrosion of the positive plate accompanying external current to that produced by local action may be approximately arrived at, either by the difference in the loss in weight experienced by the two plates, or by the amount of silver deposited. The results also show that the proportion of corrosion attending external current to that caused by local action, depends on (1) the kind of metal; (2), the kind of liquid, and on its concentration. The rate of total corrosion of the positive plate appears to be related to the degree of electromotive force. V. H. V.

**Use of Moist Electrodes.** By W. N. HARTLEY (*Chem. News*, **49**, 149).—A controversial note (comp. Abstr., 1884, 801).

**Determination of Chemical Affinity in Terms of Electromotive Force.** By C. R. A. WRIGHT and C. THOMPSON (*Phil. Mag.* [5], **17**, 282—301, and 377—391).—These papers relate to the electromotive forces set up during the interdiffusion of two liquids in a Daniell cell of a certain construction. The experiments, which are fully described, verify the following general laws:—(1.) The potential difference is increased by an increase in the strength of the solution surrounding the plate of higher potential, and diminished by an increase in the strength of the other solution. (2.) The total effect of a series of changes in the strength of the solution is equal to the algebraic sum of the effects of the several changes. (3.) The effect of a given change of strength is independent of the actual strength or nature of the solution, and of the nature of the metal immersed in it. (4.) But it varies with the condition of the surface of the metal. (5.) The E.M.F. of a Daniell cell with copper and zinc plates, both amalgamated, is practically invariable, no matter what may be the actual strength of the solutions of copper sulphate and of zinc used, provided that these are of the same molecular strength. (6.) The E.M.F. corresponds with an amount of heat greater than that developed by the intermixture of the solutions. R. R.

**Relation between Electric Energy and Radiation in the Spectrum of Incandescence Lamps.** By W. DE W. ABNEY and R. FESTING (*Proc. Roy. Soc.*, **37**, 157—173).—(Comp. Abstr., 1884, 249.)

**Relations of Heat to Voltaic and Thermoelectric Action of Metals in Electrolytes.** By G. GORE (*Proc. Roy. Soc.*, **37**, 251—290).

**The Constant of Electromagnetic Rotation of Light in Carbon Bisulphide.** By LORD RAYLEIGH (*Proc. Roy. Soc.*, **37**, 146—148).

**Measurement of the Solar Heat.** By G. FRÖHLICH (*Ann. Chim. Phys.* [6], 3, 500—540).

**New Method of Measuring the Heat of Combustion of Charcoal and Organic Compounds.** By BERTHELOT and VIEILLE (*Compt. rend.*, 99, 1097—1103).—The determination of the heat of combustion of carbon and carbon-compounds is very difficult, mainly because combustion in a current of oxygen requires a considerable time, and, moreover, is never complete. Much better results are obtained by burning the substance in oxygen under a pressure of about 7 atmos. in a calorimetric bomb (*Sur la force des matières Explosives*, i, 225). The substance is ignited by means of a metallic thread heated by an electric current. Combustion takes place in three or four minutes, and is always complete, provided that the proportion of oxygen consumed is not more than 30—40 per cent. of the original amount. If, however, more than half the oxygen is consumed, carbonic oxide and other products of incomplete combustion are found in the gases produced. This method gives the heat of combustion at constant volume, and the heat of combustion at constant pressure is obtained by making the necessary corrections.

The authors have determined the heats of combustion of cellulose and several samples of charcoal by this method with the following results:—

*Cellulose.*—The combustion of 1 gram develops 4·200 cal., and the heat of combustion (1 mol. = 162 grams) is 680·4 cal. This number agrees well with Gottlieb's determination and with the value deduced from Sarrau and Vieille's experiments on gun-cotton. It is 117·8 cal. in excess of the heat of combustion of the carbon contained in the cellulose, and it follows that the carbohydrates possess energy in excess of that calculated from the amount of carbon and water which they can yield on decomposition. The same conclusion was deduced by one of the authors from his researches on the heat developed by animal life and by fermentation.

*Charcoal.*—The following tables give the analyses of the samples of charcoal used, and their heats of combustion at constant volume:—

	C.	H.	Ash.	O.
Red charcoal, 1 ..	69·35	5·28	0·63	24·74
" " 2 ..	64·82	5·50	0·83	28·85
Black charcoal, 1.	90·13	3·37	1·76	4·74
" " 2.	90·92	3·35	1·48	4·25
Elder pith char- coal .....	70·90	5·06	2·21	21·83

	Heat of combustion, 1 gram.	Atomic heat of combustion (C = 12).
Red charcoal, 1 .....	6·660	102·02
" " 2 .....	5·970	98·5
Black charcoal, 1 ....	8·087	95·2
" " 2 ....	8·090	95·4
Elder pith charcoal....	6·105	91·5

The last column was calculated on the assumption that the oxygen was present in the form of water, and that any excess of hydrogen was in the free state. From these results, it follows that red charcoal possesses energy in excess of that corresponding with the carbon and free hydrogen which it contains, but that this excess is less than in the case of cellulose, a portion of the energy having been lost in the pyrogenic decomposition. It would seem, therefore, that pyrogenic decompositions are exothermic, a conclusion which agrees with the known complexity of these decompositions and the ease with which they take place. Charcoal obtained by the action of more regular heat, such as that of elder pith burnt inside the branch, has lost its excess of energy, whilst black charcoal obtained by the action of a high temperature approaches pure carbon in its heat of combustion. The heat of combustion of a sample of charcoal, and consequently of gunpowder made from it, cannot be calculated from the percentage composition of the charcoal, but varies with the temperature and other conditions of its mode of preparation.

C. H. B.

**Heats of Combustion of Ethereal Salts of some Fatty Acids.** By W. LOUGUINE (*Compt. rend.*, **99**, 1118—1120).—The heats of combustion were determined by the methods previously described (*Ann. Chim. Phys.* [5], 27). The following results were obtained:—

	Heat of combustion for 1 gram.	Molecular heat of combustion.
Allyl acetate. . . . .	6558.28 cal.	655,828 cal.
Diethyl oxalate ..	4905.05 „	716,203 „
Diethyl malonate. .	5378.95 „	860,632 „
Diethyl succinate. .	5791.26 „	1007,679 „

In every case, the heat of combustion of the ethereal salt is practically equal to the sum of the heats of combustion of the acid and alcohol from which it has been formed. It follows that the heat of combustion of the acid is equal to the heat of combustion of the ethereal salt, minus the heat of combustion of the alcohol. This agrees with Berthelot's earlier results (*Ann. Chim. Phys.* [5], **9**, 338). A determination of the heat of combustion of an ethereal salt may be substituted for the determination of the heat of combustion of the acid itself in cases where the latter is non-volatile or is difficult to purify.

In the last three compounds in the above table, the difference in the heat of combustion for each increment of  $\text{CH}_2$  is about 145,000 cal.

C. H. B.

**Heats of Combustion of certain Carbon-compounds.** By W. LOUGUINE (*Compt. rend.*, **100**, 63—66).—*Acetal*.—Heat of combustion for 1 gram, 7784.81 cal.; for 1 gram-molecule, 918,583.98 cal. Heat of formation, 128.0 cal. This differs by only 0.5 cal. from the sum of the heats of formation of aldehyde and ethyl ether, and hence the formation of acetal from these compounds is accompanied by a very slight thermal disturbance. There is the same difference (0.5) between the actual heat of formation of acetal and that calculated on



the supposition that it is produced by the union of 1 mol. of aldehyde and 2 mols. of alcohol, with elimination of 1 mol. of water.

*Mesityl oxide*,  $C_8H_{10}O$ .—Heat of combustion for 1 gram, 8634.06 cal.; for 1 gram-molecule, 846,137.88 cal. Heat of formation from its elements, 63.00 cal., a value 2.0 cal. higher than the heat of formation of 2 mols. of acetone minus the heat of formation of 1 mol. of water.

*Crotonaldehyde*.—Heat of combustion for 1 gram, 7747.37 cal.; for 1 gram-molecule, 542,316 cal. Heat of formation, 41.0 cal. This number is 3 cal. less than the heat of formation of 2 mols. of aldehyde minus the heat of formation of 1 mol. of water.

*Isobutyric acid*.—Heat of combustion for 1 gram, 5884.04 cal.; for 1 gram-molecule, 517,796 cal. Berthelot found for the heat of combustion of normal butyric acid, 497,000 cal.

It is important to observe that the heats of combustion are given in minor calories, whilst the heats of formation are in major calories.

C. H. B.

**Thermochemistry of Phosphorus Trifluoride.** By BERTHELOT (*Compt. rend.*, 100, 81—85).—When phosphorus trifluoride is absorbed by a dilute solution of potassium hydroxide, there is a development of heat of + 107.7 cal. per gram-molecule (88 grams). This is much lower than the heat developed by the decomposition of phosphorous bromide and phosphorous chloride under similar conditions. As a matter of fact, phosphorus trifluoride does not yield simply a phosphite and fluoride, but a fluorophosphorous acid is formed analogous to hydrofluosilicic and fluorboric acids. If it be assumed that fluorophosphorous acid is similar in composition to fluorboric acid, the simplest decomposition of the trifluoride would be represented by the equation  $2PF_3 + 3H_2O = H_3PO_3 + PF_3HF + 2HF$ . Titration of the alkaline liquid after absorption of the trifluoride (using as indicators helianthine A and helianthine B, which behave towards phosphorous acid in the same way as towards phosphoric acid (this vol., p. 348), indicates that the decomposition by alkalis takes place in accordance with the equation  $5PF_3 + 12H_2O = PF_3HF + 11HF + 4H_3PO_3$ . It is possible, however, that the nature of the decomposition varies under varying conditions, and this would explain the slight want of agreement between the individual thermochemical determinations. The results obtained by titrating the alkaline liquid also agree with the supposition that an oxyfluoride,  $POF$ , is formed.

Whatever may be the composition of the fluorophosphorous acid formed, it is a somewhat stable compound, for its potassium salt can be boiled for some time in presence of an excess of alkali without splitting up into a phosphite and a fluoride.

C. H. B.

**Thermal Equivalent of a Solution of Urea.** By M. RÜBNER (*Zeit. f. Biol.*, 20, 414—418).—The author has accurately determined, by means of two different calorimeters, the amount of heat rendered latent during solution of carbamide. He finds that the heat rendered latent by 1 gram of carbamide is equal to 61.318 calories, or for the molecule 3769 calories. In order, therefore, to arrive at the true calorific value of muscle-proteid, it becomes necessary to take into consideration

not only the calorific value of fæces and urea, but the loss of heat caused by the solution of the latter. J. P. L.

**Eutexia.** By F. GUTHRIE (*Phil. Mag.* [5], 17, 462—482).—The paper relates to substances made up of two or more constituents, in such proportions that the resultant compound (which is neither atomic nor molecular) has the minimum temperature of liquefaction. Such substances are called by the author *eutectic* (*ευ τηκειν*), and the property in question he names *eutexia*. The methods of obtaining various eutectic alloys of bismuth, lead, tin, cadmium, and zinc are detailed in the paper, the general principle being that the portion of a fused mixture that solidifies last on cooling is the true eutectic alloy. Previous experimenters have been misled by the notion that the alloy of minimum fusing point must have its constituents in some simple atomic proportions; but the author's experiments show that this is not the case, and his eutectic alloys have lower fusing points than have yet been obtained by any mixtures of the same metals.

He has applied the same methods to mixtures of fused salts that have no chemical action on each other, such as nitrates of potassium, calcium, strontium, barium, and lead. The sulphates of calcium, of barium, and of lead dissolve readily in fused potassium nitrate, and the eutectic salt alloys so formed contain in the latter case 4.6 per cent., and in the former cases nearly 1 per cent. of the sulphates.

The significance of these facts in geology and mineralogy is pointed out, and also the manner in which eutexia explains the order of solidification and disposition of the saline constituents of the earth's crust. R. R.

**Melting Points and Boiling Points as related to Chemical Composition.** By E. J. MILLS (*Phil. Mag.* [5], 17, 173—187).—The general law of chemical change first enunciated by the author that “chemical effect is directly proportional to the product of the active masses, and inversely proportional to the sum of their residues” has been expressed in the equation

$$e = \frac{\alpha \cdot xy}{x_r + y_r}$$

and in the present paper this equation is adjusted to meet the case of melting point and boiling point as related to chemical composition, heat being regarded as having the same effect as a substance entering into the reaction. The equation thus takes the following form:—

$$y = \frac{\beta(x - c)}{1 + \gamma(x - c)},$$

and is applied to the calculation of the boiling and melting points of members of organic series having the general formula  $pX \cdot xCH_2$ . The three constants of the equation are calculated from the experimental determinations in regard to three members of each series, and the values then found for the other members to which the equation is applied, approximate usually within the small portion of a degree to

the observed temperatures. The series discussed in the paper are chiefly normal paraffins, ketones, ketates, ethines, pyridines, monamines, and fatty alcohols. Certain interesting general deductions are made from the results.

R. R.

**Melting Point of Substances in Contact.** By O. LEHMANN (*Ann. Phys. Chem.* [2], **24**, 1—27).—A homogeneous solid is separated from a fluid either in the crystalline or amorphous state, the former process being discontinuous, the latter continuous; the size of the crystals formed depends on the solubility or diffusibility of the solid in the liquid. Such generalisations are based on two hypotheses: 1st, that the molecules of solids differ in kind from those of liquids; and 2nd, that a molten substance near the point of its solidification contains the solid substances in a state of solution. In the case of solidification of mixtures, there often occurs a separation into two conditions of equilibrium, leading to the formation of drops containing presumably the one substance, while the remaining solution contains the other. On the other hand, the crystallisation of a substance from a menstruum containing another, will often determine an alteration of the crystalline form of the first substance. In order to throw light on these and allied phenomena, the author has more particularly examined the appearance under the microscope of the liquefaction of two substances at their point of contact. For example, silver chloride crystallises in the trigonal form, silver iodide in octahedra, but the mixed substance when melted presents under the microscope the appearance of a dark ring; the mixture also melts at a lower temperature than either of its constituents. In other cases, such as a mixture of silver bromide and iodide, the mutual layer on cooling presents the appearance, not of an amorphous mixture, but of interlaced crystals of either substance. In the original paper, an account is given of the phenomena observed in the case of mixtures of the bromides, iodides, and chlorides, and the nitrates of various metals, as also of various organic substances. The experiments lead to the result that the mixture of the substances in the liquid state is sufficient to lower the melting point, and the mass when solidified is generally not homogeneous, but a mechanical mixture, even when the substances are isomorphous, or to some degree morphotropic.

An account is also given of experiments on the electrolysis of silver iodide, viewed under the microscope; on the passage of the current, metallic silver separates out in dendritic crystals on the negative pole, while the iodine renders the portion of salt in contact with the positive pole of a brown colour. On continuing to pass the current, the particles of silver are seen to travel towards the pole along a canal, the width of which depends on the intensity of the current, while the iodine volatilises for the greater part. The crystalline structure of the silver iodide, however, remains practically unaltered. Experiments on the electrolysis of a solution of silver iodide between electrodes of the same material are also described; during this process it appears to undergo an extension in the direction of lines of current.

V. H. V.

**Boiling Points of Saline Solutions.** By W. W. J. NICOL (*Phil. Mag.* [5], 18, 364—371).—In this paper, an account is given of some preliminary experiments on the pressures under which saturated salt solutions boil at different temperatures. The results show that increase in solubility of a salt with temperature is attended with a greater rise in boiling point, and conversely diminished solubility is accompanied by a less marked rise. The exception to the generalisation is potassium nitrate, whose solutions even of the same strength show with varied pressure a regular rise of boiling point. If, then, the solubility of the salt increases with rise of temperature, the effect of heat will be to weaken the attraction of salt for salt and of salt for water; but the diminution in the attraction of salt for salt may be so great as to be practically equal to an increase in the attraction of salt for water. Such a result probably obtains in the case of potassium nitrate mentioned above. This is not the case with constantly saturated solutions, inasmuch as the attractions of salt for water and of salt for salt respectively are in a state of equilibrium in such solutions.

V. H. V.

**Employment of Condensation in Fractionating Apparatus.** By E. CLAUDON (*Bull. Soc. Chim.*, 42, 613—617).—A comparison was made between the Winssinger and Le Bel-Henninger forms of apparatus for fractional distillation. Various mixtures of alcohol and water were simultaneously distilled in the two kinds of apparatus, care being taken that the same quantity was distilled in each in a given time, the rates being in two experiments 3 and 6 c.c. per minute. In the first-named apparatus, the alcohol came over weaker than in the second, the separation being not nearly so good at any point of the distillation, the washing of the vapour in the latter apparatus as it passes through the condensed liquid playing a very important part in the separation. By twisting a spiral of copper wire round the cold water tube in the Winssinger fractionator, an artificial condensation and washing of the vapours was set up, and experiment showed that with this modification the separation of the two liquids was greatly improved. The temperature at which different liquids distil has of course to be taken into consideration, the bulbs being surrounded with paper or wadding as the temperature rises.

J. K. C.

**Critical Volumes of Liquids.** By J. DEWAR (*Phil. Mag.* [5], 18, 210—216).—In this paper, there is described a convenient form of apparatus for demonstrating the liquefaction of oxygen. It is proposed to substitute for liquid ethylene, either solid carbonic anhydride or liquid nitrous oxide, by means of which temperatures of  $-115^{\circ}$  and  $-125^{\circ}$  respectively can be produced. At a pressure of 80—100 atmospheres, and with the means of producing a sudden expansion, the oxygen may readily be liquefied. By means of the apparatus, determinations can be made of the density of the liquefied gas by a measurement of the volume of the liquid, the volume and thus the weight of the gas given by the liquid plus vapour, and the weight of gas given by the vapour. The difference between these two last quantities corresponds with the weight of the substance in the liquid state.

A rough experiment with oxygen near the critical point gave 0.65 for the value of its density. It is pointed out that the ratio of the critical temperature to the critical pressure is proportional to the molecular volume, and a table is given of this ratio  $\frac{T}{P}$  for a number of substances, from which the following may be selected as new:—

	Critical temperature, T.	Critical pressure, P.	$\frac{T}{P}$ .
Ammonia .....	130°	115	3.5
Hydrogen sulphide.	100.2	92	4.0
Cyanogen .....	124	61.7	6.4
Methane .....	-99.5	50	3.5
Ethane .....	35	45.2	6.8

The few substances on the type of which the greater majority of compounds are built up, namely, hydrochloric acid, water, ammonia, and methane have practically the same molecular volume, whilst the more complex derivatives show an increased volume, bearing a simple relation to that of the parent substance. If the values of  $\frac{T}{P}$  be taken as proportional to the molecular volumes, then the densities of fluids at their critical temperatures can be inferred, provided that the density of one standard substance is known, for  $\frac{S'}{S} = \psi \frac{V}{V'}, \psi \frac{W'}{W}$ , where S and S' are the densities of the two substances, W W' and V V' their molecular weights and volumes respectively. Thus, taking the density of carbonic anhydride as the standard, and calculating therefrom the densities of hydrochloric acid and acetylene, the results so obtained are in accordance with the experimental results.

V. H. V.

**Method for Estimating the Specific Gravity of Solid Substances soluble in Water.** By J. L. ANDREAE (*J. pr. Chem.*, **30**, 312—315).—The author employs as the medium for this purpose a saturated solution of the substance in question, and measures the volume of a given weight of solution and excess of salt in the dilatometer described on p. 334 of this volume. A slight error creeps into this method, owing to the fact that after a change of temperature, the liquid in the capillary tube, which is not in contact with the excess of salt, is not of the same composition as that in the bulb. In the case of common salt, which was the subject of these experiments, its solubility varies so little at different temperatures, that this source of error may be neglected, but where the solubility increases rapidly with the temperature, the first reading should be made at the highest temperature. The sp. gr. of common salt was found to vary from 2.1654 at 10° to 2.1543 at 50° C.

J. K. C.

**Easy and Rapid Method of determining the Specific Gravity of Solids.** By J. J. DOBBIE and J. B. HUTCHESON (*Phil. Mag.* [5], **17**, 459—462).—A U-tube has one limb narrow and graduated; the other

wide with only a line engraved at the zero level of the graduations. The narrow limb is open; the other is fitted at the top with an air-tight cap provided with a stop-cock. Distilled water is poured in up to the zero level, the solid is dropped into the wider limb, the cap is replaced, and by blowing through the stop-cock the water in that limb is brought to its original level, when the rise of the water in the narrow limb will show the volume of water that has been displaced by the solid, whence its sp. gr. may be calculated from its previously ascertained weight. Determinations made by this method approximate very closely to determinations by the ordinary method. If the solid is lighter than water or soluble in that liquid, it is only necessary to fill the tube with some other appropriate liquid. R. R.

**Specific Gravity of Substances in the Solid State and in Aqueous Solution.** By J. A. GROSHANS (*Phil. Mag.* [5], 18, 405—416).—This paper is a continuation of the author's investigations on the relations existing between the specific gravities of compounds of analogous composition, whether in the solid state or in the state of solution (comp. Abstr., 1884, 143). Firstly, attention is called to the fact that although the specific gravities of sodium compounds in the solid state are greater than those of the corresponding potassium compounds, yet in solution this relation is reversed. Secondly, although the sp. gr. of the fluorine compounds in the solid state is greater than that of the corresponding chlorine compounds, yet the specific gravities of their solutions, provided that they are sufficiently dilute, are practically identical.

A solution may be regarded as a compound of 1 part by weight of the soluble substance with a variable number of parts by weight of water. The density of such a solution may be represented with sufficient accuracy by the formula  $d = 1 + \frac{\alpha}{aq + \beta}$ , in which  $\alpha$  and  $\beta$  are constants. In this formula the sum  $\alpha + \beta$  is of importance. Three cases are presented:—(1.) The increase of volume of the solution is exactly equal to the added volume of the water, then  $\alpha + \beta = 1$ . (2.) The increase of volume can be less than the added water, which is the ordinary case, then  $\alpha + \beta > 1$ . (3.) The volume of the solution is increased by a greater quantity than the added water, then  $\alpha + \beta < 1$ . If molecular solutions are used, then the equation will take the form  $d = 1 + \frac{V}{A + \lambda}$ , in which  $V = a/18\alpha$ ,  $\lambda = a/18\beta$ , and  $A = a/18aq$ . The results obtained by Gerlach with sugar solutions are compared with those calculated from the above formulæ. The values are concordant. If  $aq$  or  $A = 0$ , the formulæ become  $d = 1 + \frac{\alpha}{\beta} = 1 + \frac{V}{\lambda} = \delta$ , or the sp. gr. of the dissolved substance in the anhydrous state. The results calculated from the equation are, in the case of a few enumerated compounds, in agreement with the observed results.

Analogous salts of isomorphous metals such as iron, manganese, and chromium, have practically the same density when in solution,  
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and, secondly, it is possible from observations on the densities in solution of one set of salts, to deduce the densities of its analogues.

V. H. V.

**Specific Gravity of Saturated Solutions of Solid Substances at Various Temperatures.** By J. L. ANDREAE (*J. pr. Chem.* [2], 30, 305—312).—To obtain the sp. gr. of saturated solutions of various substances, two methods were employed, the first consisting in measuring the volume of a concentrated solution of known strength at various temperatures, and calculating therefrom the volume at the temperature of saturation, and the second in weighing directly a certain volume of solution saturated at a given temperature. In the first method, a dilatometer was used, consisting of a bulb with capillary graduated tube attached, the tube having three or four enlargements in its bore at various places, and being connected with a wider tube at its other extremity. Through this wider tube the salt under investigation was washed into the bulb by alternately cooling and heating the latter. After weighing the whole apparatus, immersing in a water-bath, and reading off the volume at different temperatures, the sp. gr. of the saturated solution was calculated by means of an empirical formula (comp. Abstr., 1884, 1090).

In the second method, a quantity of the saturated solution measuring a certain volume was weighed directly in a pycnometer. The only substance employed so far has been common salt, and the results of the two methods are given in the appended table:—

Temperature.	Specific gravity.		Molecular volume of NaCl.
	First method.	Second method.	
15°	1·20249	1·20253	20·96
20	1·20034	1·20034	21·21
30	1·19604	1·19601	21·62
40	1·19179	1·19174	21·93
50	1·18758	1·18749	22·16
60	1·18339	1·18328	22·32
70	1·17924	1·17912	22·39
80	1·17513	1·17499	22·41

From these figures it will be seen that the sp. gr. of saturated solutions of sodium chloride decreases with rising temperature, while the reverse is the case with the molecular volume of the same salt in saturated solution.

J. K. C.

**Density of Porous Bodies.** By G. FLEURY (*J. Pharm.* [5], 10, 255—257).—A tube 22 mm. in diameter is fitted with a narrow side tube, as in a Gay-Lussac's burette; mercury is poured in until it flows out at the side tube. The weighed piece of porous wood or other matter is then forced under the mercury by a wire, and the mercury running out is weighed.

H. B.

**Molecular Volume of Saline Solutions.** By W. W. J. NICOL (*Phil. Mag.* [5], 18, 179—193).—From experiments on the molecular volumes of certain salts of potassium and sodium, the

author has inferred that in the case of sufficiently dilute solutions, the volume of the metal is independent of its associated non-metallic radicle, and conversely the volume of the latter is independent of that of the former (comp. Abstr., 1884, 658). In this paper, this generalisation is extended to the halogen compounds of the alkali metals and alkaline earths. In the course of these investigations, it was observed that water of crystallisation has no effect on the molecular volume of a salt in solution, and a series of tables of the densities of salt solutions containing 100—400 molecular proportions of water added, are given illustrating this fact.

It is thus probable that the so-called water of constitution can be recognised in a solution of the salt, but owing to experimental difficulties this point could not be determined with exactitude. It is here suggested that water of crystallisation does not exist in solutions, for although the thermochemical investigations of Thomsen and others would tend to show that, as in a number of instances, a hydrated salt dissolves in water with absorption of heat, but when dehydrated dissolves with evolution of heat, yet it is possible that the act of solution of a dehydrated salt consists first in the taking up of water with formation of a hydrate, and subsequently this hydrate on solution parts with its water; which thus becomes indistinguishable from the rest of the water.

V. H. V.

**Cohesion Figures.** By W. v. BEZOLD (*Ann. Phys. Chem.* [2], **24**, 27—37).—It has been observed that figures similar to those of Lichtenberg can be produced by sprinkling a jelly of tragacanth with fine drops of colouring matter. In this paper, a description is given of radiating and arborescent cohesion figures formed by touching a surface of water with a pointed instrument containing an aniline dye made up with glycerol. The regularity of the radiation or arborescence depends on the relative temperature of the water and the atmosphere, and the shape of the containing vessel. For example, if a source of heat be placed on one side of the vessel the colouring drops, instead of spreading vertically down the geometrical axis of the glass, will be deflected towards the cooler side; or again, if the temperature of the water is higher than its environments, the drops spread neither vertically downwards nor radiate regularly outwards in every direction, but collected portions travel towards and then ascend the walls of the containing vessel.

V. H. V.

**Solubility and Fusibility in the Oxalic Acid Series.** By L. HENRY (*Compt. rend.*, **99**, 1157—1160, and **100**, 60—63).—The following table shows the solubility of the acids of the oxalic series in 100 parts of water:—

Oxalic acid (anhydrous) . . . . .	at 10°	5·3	parts
"      "      "      "      "      "	20	10·2	"
Malonic acid . . . . .	15	139·0	"
Succinic acid (normal) . . . . .	8·5	4·22	"
"      "      "      "      "      "	14·5	5·14	"
Pyrotartaric acid (normal) . . . .	14	83	"
Adipic acid . . . . .	15	1·44	"
		2 a 2	



Pimelic acid, the next term, is described as very soluble in water, whilst suberic ( $C_8$ ) and sebacic ( $C_{10}$ ) acids are very slightly soluble. The variations in solubility are not progressive but alternating. Acids containing an even number of carbon-atoms are only slightly soluble, whilst those containing an odd number are readily soluble. When the acids are grouped in two series, one containing those with an even number of carbon-atoms and the other those with an odd number, it is found that in each series the solubility diminishes as the molecular weight of the acid increases.

Malonic acid, intermediate between oxalic and succinic acids, differs from both of them by its much greater solubility, and this property is also common to all derivatives formed by the substitution of a hydrocarbon radicle for the hydrogen in the  $CH_2$  group in malonic acid, for example, methyl-, ethyl-, isopropyl-, and allyl-malonic acids. Methylmalonic or isosuccinic acid,  $CHMe(COOH)_2$ , is readily soluble, whilst succinic acid,  $COOH.CH_2.CH_2.COOH$ , is but slightly soluble. Fumaric acid is only slightly soluble, and corresponds with the succinic acid type, whilst maleic acid is very soluble, and corresponds with the malonic acid type. These relations are expressed by the formulæ generally given to these acids. Maleic acid is methylenemalonic acid, but the author was unable to obtain it by the action of methylene iodide on ethyl disodium malonate.

In 1877, Baeyer pointed out that in the oxalic series between  $C_4$  and  $C_{11}$ , the acids containing an even number of carbon-atoms have a higher melting point than those with an odd number, and in the odd-carbon series the melting point continually rises, whilst in the even-carbon series it continually falls.

The following table gives the melting points of the first five terms of the series, these being the only members the constitution of which is definitely known.

	Mol. wt.	Melting point.
Oxalic acid.....	90	212°
Malonic acid.....	104	132
Succinic „ .....	118	180
Pyrotartaric acid ..	132	97·5
Adipic acid.....	146	148

Examination of these numbers shows that the addition of  $CH_2$ , converting an even-carbon acid into an odd-carbon acid, lowers the melting point by about 80°, whilst the addition of  $CH_2$ , converting an odd-carbon acid into an even-carbon acid, raises the melting point about 48°. If the acids are grouped into an even-carbon and an odd-carbon series, it is found that in both the melting point is lower the higher the molecular weight, the difference for each increase of  $(CH_2)_2$  being about 32°. It would seem that these relations do not hold good amongst the higher members of the oxalic series, but the constitution of such higher members as are known, has not yet been definitely determined. Similar relations are, however, found to hold good amongst the dimethyl salts and the amides of the first three members of the series.

C. H. B.

**Salt Solutions and Attached Water.** By F. GUTHRIE (*Phil. Mag.* [5], 18, 22—35, 105—120).—In these two communications, an account is given of a continuation of the author's researches regarding the cryohydrates, with especial reference to the behaviour of ammonia and its derivatives with water.

From a solution of ammonia, no cryohydrate could be obtained, for a 33·3 per cent. solution does not crystallise at  $-80^{\circ}$ , and from more dilute solutions ice alone separates.

*Ethylamine.*—The following are some of the results obtained with solutions of ethylamine:—

Per cent. of ethylamine.	Temperature of solidification.	Nature of solid.
20	$-13\cdot3^{\circ}$	Ice.
20·64	$-13\cdot9$	Cryohydrate.
25	$-9\cdot5$	Subcryohydrate.

The last-named substance is minutely crystalline, and its solution is prone to supersaturation. The existence of these solid hydrates, formed at about  $-10^{\circ}$ , of a substance which by itself cannot be solidified in a carbonic acid freezing mixture, would tend to show that they are homogeneous entities, and not juxtapositions of independent crystals of the two constituents.

*Diethylamine* in aqueous solution gave the following results:—

Per cent. of diethylamine.	Temperature of solidification.	Nature of solid.
22	$9\cdot9^{\circ}$	Ice.
22·5	11	Cryohydrate.
23	$9\cdot9$	Subcryohydrate.
35	8	Pure solid.

*Triethylamine* in aqueous solution gave the following results:—

Per cent. of triethylamine.	Temperature of solidification.	Nature of solid.
18	$-3\cdot4^{\circ}$	Ice.
19·1	$-3\cdot8$	Cryohydrate.
20	$-3\cdot5$	Subcryohydrate.

Triethylamine possesses the remarkable property of being more soluble in cold water than in hot. Determinations are given of the critical temperature between clearness and turbidity of aqueous solutions of triethylamine, of which the following may be selected as an example: 10 parts by weight of triethylamine with 90 of water form a white emulsion which on standing separates into two distinct layers, the upper one of which is triethylamine saturated with water, and the lower water saturated with triethylamine. On heating to  $28^{\circ}$ , both layers become turbid and after some time are clarified, whilst the line of demarcation is shifted towards the centre of the mass. It is proposed to apply this property of triethylamine for the diagnosis of fevers, for a mixture of one part of triethylamine with 24·76 of water requires a temperature of  $41^{\circ}$  C., that of fever heat, to cause it to become turbid.

The radiation from an electric arc passing into an 8 per cent. solution renders it turbid, and a thin film of it spread out on glass forms a sensitive plate. Determinations are also given of the relative volumes at various temperatures of water and triethylamine, the mixture containing 46.5 per cent. of the latter.

*Salts of Aniline.*—The appended results were obtained with solutions of these salts:—

	Per cent. of salt.	Temperature of solidification.	Nature of solid.
<i>Hydrochloride</i> ..	30	— 91°	Ice.
" ..	31.86	— 10.7	Cryohydrate.
" ..	35	— 8	Salt.
<i>Nitrate</i> .....	10	— 2	Ice.
" .....	10.61	— 2.2	Cryohydrate.
" .....	10.94	0	Salt.
<i>Sulphate</i> .....	4.5	— 0.6	Ice.
" .....	4.83	— 0.9	Cryohydrate.
" .....	4.91	— 0	Salt.
<i>Oxalate</i> .....	0.14	— 1.4	Cryohydrate.
" .....	0.29	0	Salt.
<i>Salicylate</i> .....	0.24	— 0.06	Cryohydrate.
" .....	0.28	0	Salt.
<i>Pyrogallate</i> ....	20	— 2.7	Ice.
" ....	23.9	— 4.6	Cryohydrate.
" ....	33.6	0	Salt.

This last-named substance was obtained by adding aniline to pyrogalllic acid, and crystallising the product from benzene; it forms long crystals melting at 12°, soluble in water, alcohol, and ether. It turns brown on exposure to air.

*Infinite Solubility.*—From an examination of the curves of solubility of salts in water, it would appear that in some cases at a certain temperature a finite mass of water will dissolve an infinite mass of salt. In order to study the question experimentally, an alloy of potassium and lead nitrates was heated without and with small percentages of added water, and it was shown that the phenomenon of fusion, *per se*, is continuous with and is merely an exaggerated case of liquefaction by solution. Results are given of the points of solidification and the nature of the substance separated from an aqueous solution of potassium nitrate, a cryohydrate of which is formed with an 11 per cent. solution at — 3°. Attention is also drawn to the continuity in liquid condition between strong solution and anhydrous fusion in the case of potassium acetate and ammonium nitrate,\* and to the bearing of these phenomena on the determination of the melting points of organic substances. Such results also show that it may be an error to infer marine influence in the formation of rocks from the

\* The Abstractor (Trans., 1883, 374) has noted in the case of ammonium nitrate the continuity between the state of solution and that of fusion, and has attributed to this phenomenon the discrepancy in the determinations of the melting point of this salt.—V. H. V.

presence of water in them, inasmuch as obsidian, for example, if melted under pressure, will presumably mix freely with water, which, by a quick release of pressure, will be more or less vaporised.

V. H. V.

**Thermal and Volume Changes attending Mixture.** By F. GUTHRIE (*Phil. Mag.* [5], 18, 495—517).—The phenomena observed in mixtures of triethylamine and water (preceding Abstract) led the author to examine more particularly the behaviour of its homologue diethylamine. Similar results were obtained in that the liquid, at about 128—130°, was separated into two layers, although owing to the slight difference between the refractive indices of diethylamine and water, the characteristic milkiness is not observable. In connection with similar experiments on tetrethylammonium hydroxide, it is observed that even a 10 per cent. solution of this substance is decomposed at 180°, with formation of ethylene.

Experiments are also described on the thermal and volume changes produced by the mixture of alcohol, ether, carbon bisulphide, amylene, chloroform, and benzene, with each other, and as a general result it may be stated that a gain of volume is accompanied by an absorption of heat, and consequently a diminished heat-tension, and conversely, diminished volume is attended with a liberation of heat and increased tension. As an instance of the latter may be mentioned the admixture of ether with chloroform, and of the former that of chloroform with carbon bisulphide. The greatest change of volume in the case of the first pair of liquids is observable when they are mixed in monomolecular ratio ( $\text{CHCl}_3 : \text{C}_4\text{H}_{10}\text{O}$ ), and further, the increase of vapour-tension with increase of the proportion of ether is diminished at the point corresponding with this same ratio. These results would seem to point to the existence of the combination  $\text{C}_4\text{H}_{10}\text{O}, \text{CHCl}_3$ . Similar experiments with chloroform and carbon bisulphide pointed to the formation of a similar compound,  $\text{CS}_2, \text{CHCl}_3$ . Ethyl iodide and bromide when mixed together present a case of almost absolute non-interference, inasmuch as the vapour-tension of such a mixture decreases regularly with increased proportion of ethyl iodide.

V. H. V.

**Thermal Relationship between Water and Certain Salts.**

By B. ILLINGWORTH and A. HOWARD (*Phil. Mag.* [5], 18, 123—127).—As the study of the relationship of the homologous salts of a series of acids towards water might throw light upon the general relation between salts and water, as regards the formation of cryohydrates, the authors have observed the temperatures at which potassium methyl, ethyl, and amyl sulphates form cryohydrates. The results were as follows:—

Salt.	Temperature of the cryogen.	Water per cent.
Potassium methyl sulphate....	— 11·3°	60·16
„ ethyl sulphate ....	— 13·9	54·99
„ amyl sulphate ....	— 5·0	73·97

The methyl compound is thus intermediate between the ethyl and the amyl compounds. Determinations of the sp. gr. of these salts at

19.6° gave potassium methyl sulphate = 2.097; potassium ethyl sulphate = 1.843; and potassium amyl sulphate = 1.144. The specific gravities of these salts are thus regularly in the inverse order of their molecular weight. V. H. V.

**Laws of Solution.** By H. LE CHATELIER (*Compt. rend.*, 100, 50—52).—A mathematical application of the laws of chemical equilibrium (this vol., p. 117) to the case of the dissolution of salts in water. C. H. B.

**Saturation of Salt Solution.** By W. W. J. NICOL (*Phil. Mag.* [5], 17, 537—550).—In a former paper (Abstr., 1884, 253), the author put forward the theory that the saturation of a salt solution obtains when the sum of the attraction of the individual salt molecules for one another is equal to the sum of the attraction of the water for the salt molecules. In this connection, it is presumable that the attraction of the heterogeneous molecules of water and salt respectively is one cause of the contraction attending the solution of the salt, whilst conversely the attraction of the homogeneous molecules of the salt has an opposite effect. If then this theory were a correct representation of the phenomena in question, larger molecular volumes are due to an attraction of a weaker kind between homogeneous molecules of salt, and a greater solubility would thus result. From experiments on the chlorides and nitrates of potassium and sodium, it is to be concluded that the more soluble a salt is in any liquid, the more nearly will its molecular volume in the solid state and in a state of solution approximate. Instances are adduced to show that diminished molecular volume is attended with diminished solubility, and this, whether the composition of the salt remains unchanged or not. Experiments are also detailed regarding the saturation of two salts dissolved simultaneously, which tend to show (1) that each salt dissolves independently of the other, and (2) that each salt increases the solubility of the other, not by any tendency to form homogeneous combinations, but rather by a mechanical interposition of the molecules of the two salts with those of water. V. H. V.

**Reciprocal Solution of Liquids.** By W. ALEXÉEFF (*Bull. Soc. Chim.*, 42, 329).—With liquids between which no chemical reaction occurs, the solubility of the liquid possessing the greater cohesion is higher in the liquid having the less cohesion, than the solubility of the liquid of less cohesion in that of greater cohesion. Where, however, there is a tendency to chemical reaction, this rule does not apply. Thus at 0° the solubility of paraldehyde in water is greater than that of water in paraldehyde, but at higher temperatures where the compound is decomposed, the inverse of this occurs, and constitutes a particular case of the law. With liquids having a tendency to combine, as well as to dissolve, there are two limits to reciprocal action. At temperatures above which the liquids mix in all proportions, a homogeneous liquid is formed as a result of "solubility," but at lower temperatures a compound is produced through the agency of "affinity." W. R. D.

**Lines of no Chemical Change.** By E. J. MILLS and W. M. MACKEY (*Phil. Mag.* [5], 16, 429—433).—If zinc is acted on by diluted sulphuric acid of a percentage strength expressed by  $y$ , a quantity of hydrogen gas will be given off which may be represented by  $x$ , and will vary with  $y$ , so that one may be represented mathematically as a linear function of the other, thus:—

$$y = a + bx + cx^2.$$

From three experiments made under conditions described in the paper, the values of the constants  $a$ ,  $b$ , and  $c$  are calculated; then  $x$  in the equation is put  $= 0$ , and  $a$  should then represent a certain percentage strength of the sulphuric acid with which the zinc will not be acted upon, the temperature being the same as in the three determining experiments. The results laid down as a curve, in which the ordinates represent the strength of the acids, whilst the abscissae represent the temperature, gave a line of "no chemical action" which up to  $35.25^\circ$  forms a hyperbolic curve; higher temperatures furnish a second hyperbola tending to symmetry with the first, and touching it at a point corresponding with the percentage strength of 79.62. An experiment was made with acid of 76.55 per cent. at the corresponding temperature, and a very slight, though distinct, evolution of gas took place. The reaction between diluted sulphuric acid and zinc is thus shown to be very complicated; for with strengths of 58.77 to 79.62 per cent. there are two temperatures of no chemical change, and between 54.47 and 57.77 there are four such temperatures. R. R.

**Rate of the Chemical Absorption of Gases.** By J. J. HOOD (*Phil. Mag.* [5], 17, 352—367).—The object of the investigations recorded in this paper was to obtain an estimate of the rates of interdiffusion in atmospheres of air and of hydrogen respectively, of hydrogen sulphide, carbonic anhydride, chlorine, and sulphurous anhydride. The results were obtained by observing the rapidity with which the several gases were taken up by chemical absorbents. It was found that the rate at which each gas is absorbed is less when it is mixed with air than when it is mixed with hydrogen. In both atmospheres, hydrogen sulphide is absorbed more rapidly than carbonic anhydride, and sulphurous anhydride than chlorine; yet these last are each absorbed much more rapidly than either of the former, especially in an atmosphere of air. When hydrogen is used, hydrogen sulphide and chlorine are absorbed with nearly equal rapidity. R. R.

**Correction of the Numerical Results given in a former Paper on Compressed Gas Manometers.** By E. H. AMAGAT (*Compt. rend.*, 99, 1153—1154).

**Combination of Gases.** By J. J. THOMSON (*Phil. Mag.* [5], 18, 233—267).—According to the doctrine of Clausius and Williamson, the individual atoms forming the molecules of a compound gas are continually changing partners; its consequences can thus be developed by mathematical analysis. In this memoir, an attempt is made in this direction, particularly as regards the effects producible by time,

pressure, temperature, and the relative masses of the substances undergoing chemical change. In order to form a definite mental presentation of these phenomena, it is here assumed that the constituent atoms consist of one or more vortex rings. In a former work, the author has shown that when two vortex rings of equal strength in approximately parallel planes, perpendicular to the lines joining the centres, are moving in the same direction, and the conditions are such that the hinder ring overtakes the one in front, they coalesce, the lines of vortex core remaining approximately constant. Such a union or pairing together of vortex rings may take place in the combination of atoms, whether of the same or different kinds, to form molecules. If, under these circumstances, the paired vortex rings are subjected to some disturbing influence, their radii will be changed by different amounts; the velocities of translation will thus become different and separation will occur. In the case of a permanent homogeneous molecule, it is necessary that the mean time during which an atom is paired with another atom, of the same or different kind, which is here called the paired time, should be large as compared with the time during which it is alone, and free from other atoms, which is here called the free time. An external disturbance will diminish this ratio, and provided it be of sufficient magnitude, the value of the ratio will be so much diminished that the substance will no longer exhibit the properties of a homogeneous chemical entity, but of its constituent elements. Further, if the value of the ratio of the free to the paired times be very small, the gas possessing this characteristic will not readily enter into chemical reactions; nitrogen may be an example of this kind. It is thus evident that the energy of a gas, and therefore the temperature, depends on the mean radius of the vortices which form its constituent atoms, and conversely the mean radius is a function of the temperature. Unless, then, the atoms do not remain long together after the coalescence of the vortices, chemical combination will not readily take place.

This theory of the vortex rings offers a more particular explanation of the combination of the constituent atoms in a molecule, or under altered conditions, of their reverse decomposition. For if in such a coalescence as described above, there are forces which tend to make the velocity of the front less than that of the hinder ring, the two will tend to combine more closely; if the converse phenomenon takes place, the two rings will tend to move further apart, the result of which will be decomposition. These doctrines are illustrated by mathematical analysis, and the case is supposed of the dissociation of molecules of a gas containing two atoms, under such a condition that the initial violence of the chemical change is moderated. If  $t$  be proportional to the mean paired time of the atoms and  $\tau$  proportional to the mean free time, let  $m$  be the molecules at any given time,  $n$  the atoms at the same time; then if the gas be in a closed vessel,  $n+2m$  will be constant and equal to  $N$ , the number of atoms if all the molecules were dissociated. Then  $\tau$  will be inversely proportional to  $n$ , let it equal  $\frac{\tau}{n}$ . In the time  $\delta t$  the number of molecules split up is equal to  $m\delta t/t$ , the number of pairs of atoms which combine in the

same time  $\delta t = n\delta t/t = n^2\delta t/\tau$ ; so that if  $\delta m$  is the increase in the number of molecules in the time  $\delta t$ , then  $\delta m = \frac{n^2\delta t}{\tau} - \frac{n}{t}\delta t$  or  $\frac{dm}{\delta t} = \frac{n^2}{\tau} - \frac{n}{t}$ ; similarly  $\frac{dn}{\delta t} = \frac{2m}{t} - \frac{2n^2}{\tau}$  (I). When things have got into a stationary state,  $\frac{dm}{\delta t}$  and  $\frac{dn}{\delta t}$  vanish, so that  $\frac{n^2}{\tau} = \frac{m}{t}$  (II); and  $n + 2m = N$ , then  $n + \frac{2t}{\tau}n^2 = N$ ; if the dissociation is slight, so that the number of atoms is small as compared with that of the molecules, then  $\frac{2tn^2}{\tau} = N$ . This last equation can be represented in terms of

the density of the mixed gas; for if  $\Delta$  be the vapour-density of the dissociated gas,  $D$  the density of the gas not dissociated, then 
$$\frac{\Delta}{D} = \frac{\frac{N}{2}}{n+m} = \frac{N}{N+n} \text{ or } \frac{n}{N} = \frac{D-\Delta}{\Delta}.$$
 If  $p$  be the pressure of the gas,  $p = CN$  where  $C$  is a constant, and substituting for  $n$  and  $m$  in equation (II), then  $(D-\Delta)^2 = \frac{\tau}{tCp} \left( \frac{2\Delta-D}{2} \right) \Delta$ . In accordance with

this equation, the author compares the calculated with the observed values for the vapour-density of iodine partially dissociated at  $1250^\circ$ ; the difference between them might be accounted for by experimental errors. Similar but more complex mathematical reasoning is applied to cases of decomposition and subsequent recombination such as that of phosphorus trichloride and chlorine, or of the compound of methyl oxide and hydrochloric acid investigated by Friedel (*Bull. Soc. Chim.*, 1875, 160; 1876, 241), and the observed and calculated values are found to be in accordance. As a still more complex case, the combination of hydrogen with chlorine, is investigated, which presents five systems of particles, the atoms and molecules of hydrogen, the atoms and molecules of chlorine, and the molecules of hydrochloric acid, and an equation deduced to find the quantity of hydrochloric acid produced when hydrogen and chlorine are mixed in any proportions. Although this particular case has not been investigated, yet the analogous instance of the combination of hydrogen with iodine has been examined by Lemoine, whose results agree with those calculated by the author's theory. Cases are also examined in which gases A, B, C, mixed in a closed vessel and exploded, can form the combinations AB and AC respectively, but B and C cannot combine; such are the combinations by explosion of oxygen with carbonic oxide and hydrogen. From the equation deduced, it follows that the ratio of the quantity of water formed to the quantity of carbonic anhydride bears a constant ratio to that between the quantities of hydrogen and carbonic oxide left unaltered. This *à priori* deduction agrees with the experimental deduction of Horstmann. Similar principles may be applied to other cases of gaseous combination, and much of the reasoning would seem to be applicable to liquids, although the want of knowledge of the molecular composition of liquids presents difficulties in the reasoning of such cases on direct dynamical principles.



**The Numerics of the Elements.** By E. J. MILLS (*Phil. Mag.* [5], 18, 393—399).—In this paper it is shown that the “numerics” or numbers representing the atomic weights of the elements can be determined by the equation  $y = p15 - 15(0.9376)^x$ , in which  $y$  is the atomic weight,  $p$  and  $x$  are factors. Tables are given in which the calculated values are compared with those given in the treatises of Clarke and Meyer and Seubert. These results are opposed to Prout’s theory of integral multiples, for this could only hold good in the few cases in which  $x = 0$  or  $\infty$ .  
V. H. V.

**The Periodic Law.** By T. CARNELLEY (*Phil. Mag.* [5], 18, 1—22).—In this paper, certain relations between the melting and boiling points and heat of formation of the halogen compounds of the elements are given in illustration of the periodic law. The general results may be summed up as follows:—(i) If in a series of binary normal compounds one element is common to all, the melting points, boiling points, and heats of formation are periodic functions of the atomic weight of the other element; (ii) the influence of the halogen on these physical properties increases with the number of atoms in the compound; (iii) in normal halogen compounds, the influence of either of the elements on the melting or boiling point increases with the atomic weight of the one, but decreases with the atomic weight of the other element. The numerical relations existing between the melting points and boiling points of the halogen compounds of the elements, are detailed at length in the original memoir, and serve as a means of calculating or even predicting these points within certain limits, and of applying the results obtained for the classification and determination of the atomic weights of the metals. Numerous examples are given of the application of these several processes.

V. H. V.

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## Inorganic Chemistry.

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**Hydrogen Peroxide.** By HANRIOT (*Compt. rend.*, **100**, 57—60 and 172—175).—A 5—10 volume solution of hydrogen peroxide, that is, a solution capable of giving off 5 to 10 times its own volume of free oxygen, can be boiled without sensible decomposition, but when the strength reaches 12 vols. decomposition commences. If, however, the hydrogen peroxide is very pure, decomposition is so slow that the solution can be concentrated on a water-bath until it attains a strength of 15 vols.

When a dilute solution of hydrogen peroxide is partially frozen by placing it in a mixture of ice and salt, the portion which remains liquid contains a much higher proportion of the peroxide, whilst the bulk of the solid portion is practically pure ice. If, however, the ice is slowly melted, the liquid which first forms is very rich in hydrogen peroxide, and this would seem to indicate the existence of a hydrate

melting between  $-13^{\circ}$  and  $-15^{\circ}$ . By successive freezings the peroxide can be concentrated until it has a strength equal to 70 vols., but beyond this point it no longer freezes at  $-13^{\circ}$ . By using methyl chloride as a refrigerator, however, the hydrogen peroxide can be frozen at  $-15^{\circ}$ , and concentration can be carried to 140 vols. or even further, but the process becomes tedious and troublesome. The main difficulty in this method of concentration is the separation of the mother-liquor from the crystals of ice.

Dilute solutions of hydrogen peroxide are best prepared by the action of hydrofluoric acid on barium peroxide carefully freed from soluble salts. The peroxide solution thus obtained is made distinctly alkaline by adding baryta-water, and barium peroxide and any iron or manganese are thus precipitated. The solution is then acidified with sulphuric acid, and the hydrogen peroxide concentrated first on a water-bath and then by successive freezings. The advantage of this method is that the hydrogen peroxide is obtained in a high state of purity, and therefore is much less liable to decompose in the process of concentration.

If a solution of hydrogen peroxide is distilled under a pressure of 30 mm. of mercury, the amount of peroxide which passes over is greater the higher the concentration of the solution. If commercial hydrogen peroxide (10–12 vols.) is distilled in a vacuum, practically no hydrogen peroxide passes over until the liquid in the retort is reduced to about one-fifth its original volume. At this point, the fractionating bulbs are removed, and the distillation continued in a vacuum until the liquid in the retort begins to decompose. More water is then added, and distillation continued. The strength of the distillate obtained in this way corresponds with 5–8 vols., and it is concentrated in a vacuum until decomposition commences. By concentration under a pressure of 30 mm., a 267 vol. solution can be obtained. Hydrogen peroxide undergoes no decomposition whatever when distilled, provided the concentration of the solution in the retort is no higher than that corresponding with 150 vols.

*Estimation of Hydrogen Peroxide.*—The volume of oxygen evolved when the solution is boiled gives no exact measure of the amount of hydrogen peroxide present, for a considerable proportion of the latter volatilises without decomposition. When the hydrogen peroxide is decomposed by manganese dioxide, a certain quantity always escapes decomposition, but the error is constant, and corresponds with 0.3 vol. If this correction is made, the results are exact.

Pure hydrogen peroxide has an acid reaction. Even if a solution is made alkaline with baryta and boiled, the vapour of hydrogen peroxide reddens litmus. It is evident that Thenard's *neutral* hydrogen peroxide must have contained a small quantity of baryta, and hence its instability. The vapour of hydrogen peroxide has a distinct odour, recalling that of nitric acid. Hydrogen peroxide conducts electricity better than pure water, and can be electrolysed without addition of acid, large quantities of oxygen being given off at the positive electrode. At the same time, a small quantity of a mixture of oxygen and hydrogen, in proportions varying with the duration of the experiment, is given off at the negative pole. The current decomposes hydrogen

peroxide into oxygen and water. It cannot be admitted that the hydrogen peroxide is reduced by hydrogen liberated from the water at the negative pole, for if the solution is acidified, hydrogen is evolved at the negative pole and the peroxide is not reduced.

C. H. B.

**Iodic Anhydride.** By K. WEHSARG (*Ber.*, **17**, 2896—2897).—The author passed mixtures of iodine and oxygen through tubes, containing platinised asbestos and heated at 200°, 250°, and 300° respectively, but no combination took place. No better results were obtained when similar mixtures were heated with spongy platinum in a Hofmann vapour-density apparatus at 192° (? by dimethylaniline vapour), or in closed tubes at 200°, 250°, or 300°. It therefore appears, that although the heat of formation of iodic anhydride is positive (Thomsen gives  $I_2 + O_3 = 44.860$  cal.), iodine does not combine directly with oxygen, even in the presence of spongy platinum or platinised asbestos.

L. T. T.

**Allotropic Transformation of Sulphur at very Low Temperatures.** By J. M. RUYLS (*Chem. Centr.*, 1884, 449).—Fused sulphur was exposed for several days to a temperature varying between  $-39.5^\circ$  and  $-11.2^\circ$ . A change of colour was noticed at the edges soon after solidification had taken place, whilst the mass remained unaltered for some days; small yellow spots then appeared, which gradually became larger and brighter in colour until after twelve days the whole mass had changed into the rhombic modification. A second experiment in which the temperature varied between  $-38.4^\circ$  and  $-4.8^\circ$  gave similar results.

A. K. M.

**The Temperature of Allotropic Transformation of Sulphur.** By L. T. REICHER (*Chem. Centr.*, 1884, 450).—The author finds that the temperature of the allotropic transformation of sulphur is  $95.6^\circ$ . Below this temperature, monoclinic sulphur suffers a diminution in volume, above it rhombic sulphur experiences an increase in volume, whilst at the temperature of change both modifications have a constant volume. In these experiments, the pressure was equal to four atmospheres. At a pressure of 15 atmospheres, the temperature of transformation was raised to  $96.2^\circ$ , indicating a difference of  $0.05^\circ$  for one atmosphere pressure.

A. K. M.

**Preparation of Hydrogen Sulphide.** By H. N. DRAPER (*Chem. News*, **50**, 292).—Two two-necked Woulff's bottles are each fitted with corks, and a long and a short glass tube bent at right angles. One of the bottles contains ammonium sulphide, which more than covers the end of the long tube, the other contains dilute sulphuric acid (1 of acid to 4 of water) to a somewhat greater height. The ammonium sulphide bottle is connected by means of its short tube with the long tube of the other bottle. For use, a gentle current of air is forced through the ammonium sulphide, it passes through the sulphuric acid bottle, and escapes from its short tube mixed with hydrogen sulphide. No free ammonia passes the acid liquid, nor is there any sulphur deposited in it. When not in use, there is no

escape of hydrogen sulphide, and the introduction of a stop-cock between the bottles prevents the diffusion of the ammonium sulphide vapour into the acid. The author considers that forcing the vapour of fuming hydrochloric acid into sodium sulphide solution may probably give a good result.

D. A. L.

**Purification of Sulphuretted Hydrogen from Arsenic.** By O. V. D. PFORDTEN (*Ber.*, **17**, 2897—2903).—The author recommends passing the impure gas over potassium polysulphide, heated at 350—360°. A glass tube about 30 cm. long is filled with pieces of liver of sulphur and heated by means of an air-bath, in the ends of which are holes just large enough to push the tube through. The temperature of the air-bath is kept at 350—360°. The previously dried sulphuretted hydrogen is passed through this tube, and finally through a wash-bottle containing a solution of sodium carbonate. Sulphuretted hydrogen, prepared from crude materials containing arsenic, is entirely freed from arseniuretted hydrogen by this process, and may be used with safety in forensic investigations. The author believes the result obtained to be due to the reaction  $2\text{AsH}_3 + 3\text{K}_2\text{S}_3 = 2\text{AsS}_3\text{K}_3 + 3\text{H}_2\text{S}$ .

L. T. T.

**Spontaneous Oxidation of Sulphur.** By E. POLLACCI (*Chem. Centr.*, 1884, 484).—It has long been known that when sulphur is mixed with water and exposed to the air at a temperature of 35—40°, oxidation takes place with formation of sulphuric acid. The author concludes from his experiments that the oxidation is due to atmospheric oxygen, and not to the decomposition of water as is sometimes stated. It is found that water free from air may remain for months in contact with sulphur without the formation of an appreciable quantity of sulphuric acid. Nascent oxygen effects the oxidation much more readily than ordinary oxygen, whilst ozone is probably the active constituent of the air.

A. K. M.

**Electrolytic Preparation of Nitrogen Chloride.** By F. MARECK (*Chem. Centr.*, 1884, 481—482).—The following phenomenon was observed whilst passing an electric current through a concentrated solution of ammonium chloride covered with a thin layer of turpentine. On passing a strong current through the solution so as to produce a rapid series of detonations, and then quickly removing the platinum electrode, this was found to be covered with a slight grey coating, but if the current be allowed to pass for 8—10 minutes and the platinum then removed, a dense soot-like deposit is found, which, however, gradually vanishes, like condensed moisture (from the breath) from polished steel, and during this vaporisation a distinct odour of ammonia is observable. When dipped into dilute acid, the precipitate vanishes almost instantaneously. If mercury be poured upon the coated platinum it spreads as it does on zinc when wetted with acid.

A. K. M.

**Crystallisation of Phosphoric Acid.** By P. L. HUSKISSON (*Pharm. J. Trans.* [3], **14**, 644—645).—Solutions of phosphoric acid

of sp. gr. less than 1.660 cannot be crystallised by any means at ordinary temperatures; whilst solutions of higher sp. gr. under similar conditions can only be crystallised by the introduction of a crystal of orthophosphoric acid. Phosphoric acid of sp. gr. 1.800, however, crystallises when exposed in a vacuum over sulphuric acid. The crystals obtained in this manner will not start crystallisation in solutions of lower sp. gr. than 1.800, and on the other hand the crystals from the weaker solutions will not induce crystallisation in the stronger acid.

D. A. L.

**Saturation of Phosphoric Acid by Bases.** By A. JOLY (*Compt. rend.*, **100**, 55—57).—The author has previously pointed out (*Abstr.*, 1882, 926,) that when "helianthin," or Poirrier's Orange No. 3, is used as an indicator, one molecule of phosphoric acid is neutralised by one equivalent of an alkali. If, however, phenolphthaleïn is used as an indicator, two equivalents of alkali are required to neutralise a molecule of phosphoric acid. This is a striking example of the fact that the "neutrality" of a salt formed by the union of a strong acid with a strong base, depends on the nature of the indicator employed.

The difference in the behaviour of these indicators may be employed as a means of estimating the amount of phosphoric acid and of a monobasic acid, such as hydrochloric acid, which is neutralised by one equivalent of alkali when they exist together in the same solution, for instance, in the solution obtained by the action of water on the chlorides of phosphorus. A given volume of the liquid is titrated with helianthin as indicator, and then an equal volume is titrated with phenolphthaleïn as indicator. If  $x$  and  $y$  represent respectively the volumes of alkali required to neutralise the phosphoric and hydrochloric acids separately, and  $V$  the total volume of alkali required by the mixed acids when helianthin is the indicator, then—

$$V = x + y,$$

and if  $V'$  represents the volume of alkali required when phenolphthaleïn is the indicator, then—

$$V' = 2x + y,$$

and from these two equations the amounts of phosphoric and hydrochloric acid can be readily calculated.

C. H. B.

**Atomic Weights of Carbon, Phosphorus, Tin, and Zinc.** By J. D. VAN DER PLAATS (*Compt. rend.*, **100**, 52—55).—*Carbon.*—Ceylon graphite, purified by the usual methods; carbon from sugar, purified by heating in chlorine; and carbon from Schleicher and Schüll's purified filter-paper, were burnt in oxygen gas and the carbonic anhydride weighed, the necessary corrections being made for the ash and hydrogen contained in the carbon. The mean of six determinations is  $C = 12.0028$ , the extremes being 12.0010 and 12.0053.

*Phosphorus.*—Three methods were employed, namely:—(1.) The precipitation of silver from a solution of silver sulphate by phosphorus which had been twice distilled in nitrogen; (2) the analysis of silver

phosphate; and (3) the oxidation of ordinary phosphorus in oxygen under low pressure. The mean of two determinations by each method gives  $P = 30.975$ .

*Tin*.—Purified tin was converted into stannic oxide by the action of nitric acid; and stannic oxide, obtained by fractional precipitation of a solution of stannous chloride by exposing it to the air, was reduced in a current of hydrogen. Three determinations by the first method give  $Sn = 118.08$ , and four determinations by the second method give  $Sn = 118.07$ .

In all the above calculations  $O = 16$  and  $Ag = 107.93$ .

*Zinc*.—Zinc obtained by reducing the oxide in hydrogen or by electrolysis of the sulphate, was dissolved in dilute sulphuric acid, and the volume of the liberated hydrogen determined. The mean of the three determinations is  $Zn = 65.18$ .

The author points out that the value of the relation  $O : H$  is still uncertain by 0.5 per cent.

C. H. B.

**Preparation of Sodium Sulphide.** By A. DAMOISEAU (*J. Pharm.* [5], 10, 351—352).—The best yield is obtained when 45 parts of soda in solution are saturated with sulphuretted hydrogen, the solution being allowed to become warm; a solution of 55 parts of caustic soda is then added, and the whole allowed to crystallise.

H. B.

**Molecular Modifications of Silver Bromide.** By DE PITTEURS (*Chem. Centr.*, 1884, 411—412).—The knowledge of the molecular modifications of silver bromide has been very much extended by the gelatin process of photography. The different modifications, although apparent to the eye, become more sharply distinguishable by their unequal sensitiveness to light. The following table exhibits the differences which exist in the appearance and behaviour of various silver bromide films:—

By transmitted light.		By reflected light.	
Semi-transparent	orange..	slate-blue ....	Most fresh collodion emulsions.
		bluish-white ..	Older bromide of silver collodion. Wet plates.
	reddish-orange	bluish-white ..	Very sensitive wet collodion.
		yellowish-white	Very old bromide of silver collodion.
Almost opaque	violet-blue	yellowish-white	Very sensitive ditto.
		greenish-yellow	Bromide of silver gelatin of medium sensitiveness.
	blue....	green or violet-green	Very sensitive ditto.
		indistinct ....	Very slightly sensitive bromide of silver collodion, yielding indistinct pictures, and those affected by the red end of the spectrum.

The most sensitive varieties of silver bromide consist of coarse grains, and, therefore, yield inferior negatives. P. F. F.

**Combination of Silver Chloride, Bromide, and Iodide with Colouring Matters.** By M. CAREY LEA (*Chem. News*, **51**, 30—31).—A considerable number of colouring matters combine with silver haloïd salts. The colouring matters most frequently impart to these silver salts their own shade or something approaching it; but this is not always the case, for sometimes the colour of the silver salt differs considerably from that of the colouring matter; and, moreover, each of the three haloïd salts may be coloured differently by one and the same dye. For example, silver bromide, precipitated from the nitrate in presence of aniline-purple is coloured purple; with cardinal-red it is coloured bright flesh or salmon colour; with naphthalene-yellow, light yellow; with eosin, pinkish or salmon colour. Different specimens of the same dye sometimes give different colours, for example, bluish-green and purple silver bromide have been obtained from different samples of methyl-green. The author refers to the use of these facts in photography, and points out that they are in many cases opposed to Vogel's theory, that sensitive films stained with these colouring matters gain sensitiveness for those rays of the spectrum which the uncombined colouring matter absorbs. D. A. L.

**Purification of Mercury by Distillation in a Vacuum.** By J. W. CLARK (*Phil. Mag.* [5], **17**, 24—27).—Mercury is distilled in the Torricellian vacuum, and condensing, feeds at the top the barometric column, while the metal runs out at the same rate from the upturned lower end of the tube. The paper is accompanied by a plate representing the apparatus. R. R.

**Solubility of Mercuric Iodide in Water and Alcohol.** By E. BOURGOIN (*Bull. Soc. Chim.*, **42**, 620—622).—1 litre of distilled water at 17·5° dissolves 0·0403 gram mercuric iodide; the solution is tinged brown with sulphuretted hydrogen and deposits mercuric sulphide after a lapse of time. At 22°, water dissolves 0·0536 gram per litre. The iodide is much more soluble in alcohol; absolute alcohol dissolves 11·18 grams per litre; 80 per cent. alcohol, 2·857 grams per litre; and 9 per cent. alcohol, 0·086 gram per litre at 18°.

J. K. C.

**The Rare Earths.** By A. v. WELSBACH (*Monatsh. Chem.*, **5**, 508—522).—A detailed description of the methods and operations employed in extracting cerium, didymium, and lanthanum from cerite.

P. P. B.

**Double Sulphide of Aluminium and Potassium.** By D. GRATAMA (*Chem. Centr.*, 1884, 452).—St. Claire-Deville described a double sulphide of aluminium and potassium, which was obtained by passing sulphur vapour over a strongly ignited mixture of carbon with potash-alum; the product decomposed water with violence. The author has repeated this experiment and obtained a substance which is spontaneously inflammable, yields no gas with pure water, and only a slight evolution of hydrogen sulphide when treated with hydro-



chloric acid. The filtered solution contained no aluminium, showing that no double sulphide had been formed. The experiment has been repeated at higher temperatures, but in no case was the compound sought for obtained. A. K. M.

**Tricobalt Tetroxide.** By A. GORGEU (*Compt. rend.*, **100**, 175—177).—Tricobalt tetroxide is obtained in the same way as artificial hausmannite (Abstr., 1883, 859), by the action of moist air on cobalt chloride at a red heat. Measurable crystals separate in rings on the sides of the crucible above the fused salt, and are washed with water. They are free from chloride, and approach more nearly in composition to  $\text{Co}_3\text{O}_4$ , the lower the temperature at which they have been formed. The percentage of oxygen is usually about 24—24·5 instead of 26·5. There is little doubt, however, that the crystals have the true form of  $\text{Co}_3\text{O}_4$ . When this oxide is heated to bright redness, it gradually loses oxygen, and is converted into the monoxide  $\text{CoO}$ , the decomposition being perfectly continuous. When the monoxide is heated in presence of air, it absorbs oxygen up to a dull red heat, but at higher temperatures the oxygen is again partially expelled.

The crystals of  $\text{Co}_3\text{O}_4$  are quadratic octahedra, without modifications, but the angles are very different from those of hausmannite (*loc. cit.*), and hence it follows that trimanganese tetroxide and tricobalt tetroxide are not isomorphous. C. H. B.

**Basic Salts.** By J. HABERMANN (*Monatsh. Chem.*, **5**, 432—450).—This is an account of the results of the investigation of basic compounds, of which a short notice has already appeared (Abstr., 1884, 151). Basic sulphates, chlorides, and nitrates, of the metals copper, nickel, cobalt, zinc, and cadmium, have been prepared.

These compounds are obtained by adding dilute ammonia to a boiling solution of the normal salt of the metal, as long as any precipitate is obtained; in this manner, the following compounds have been produced:—*Basic copper sulphate*,  $7\text{CuO}, 2\text{SO}_3 + 6\text{H}_2\text{O}$ , is a finely granular bluish-green powder, insoluble in cold water; when heated to dull redness it forms a black compound of the formula  $7\text{CuO}, 2\text{SO}_3$ . *Basic copper nitrate*,  $4\text{CuO}, \text{N}_2\text{O}_5 + 3\text{H}_2\text{O}$ , is a light blue granular non-crystalline powder; it is insoluble in water, but is converted into a dark powder when boiled with it. *Basic copper chloride*,  $\text{CuCl}_2, 3\text{CuO} + \frac{3}{2}\text{H}_2\text{O}$ , is a bluish-green powder, not acted on by water. It seems to be identical with the compound obtained by Reindel from copper sulphate, sodium chloride, and ammonia, and has a composition similar to that of some specimens of atacamite, analysed by Debray and Kraut (*Gmelin-Kraut*, **3**, 644). *Basic nickel sulphate*,  $7\text{NiO}, \text{SO}_3, 7\text{H}_2\text{O} + 3\text{H}_2\text{O}$ , is a yellowish-green powder, sparingly soluble in water; it has an alkaline reaction, and absorbs carbonic anhydride from the air. *Basic nickel nitrate*,  $3\text{NiO}, 2\text{N}_2\text{O}_5 + 5\text{H}_2\text{O}$ , is a light whitish-green powder, completely insoluble in either cold or hot water. The basic chloride has not been obtained in a pure state. *Basic cobalt sulphate*,  $5\text{CoO}, \text{SO}_3$ , is obtained as a blue flocculent precipitate, which loses water completely at  $288\text{—}292^\circ$ , forming a brownish-black powder. *Basic*

*cobalt nitrate*,  $4\text{CoO}, \text{N}_2\text{O}_5 + 6\text{H}_2\text{O}$ , forms a blue precipitate, which absorbs oxygen to form a green compound. *Basic cobalt chloride*,  $\text{CoCl}_2, 3\text{CoO} + 3\frac{1}{2}\text{H}_2\text{O}$ , is a peach-coloured precipitate, which is hygroscopic, but insoluble in hot and cold water. *Basic zinc sulphate*,  $4\text{ZnO}, \text{SO}_3, 3\text{H}_2\text{O} + 2\text{H}_2\text{O}$ , is a white crystalline powder, which loses  $2\text{H}_2\text{O}$  at  $100^\circ$ . The remainder of the water is expelled at a considerably higher temperature. *Basic zinc nitrate*,  $5\text{ZnO}, \text{N}_2\text{O}_5 + 5\frac{1}{2}\text{H}_2\text{O}$ , and the *chloride*,  $2\text{ZnCl}_2, 9\text{ZnO} + 12\text{H}_2\text{O}$ , are both white crystalline compounds.

The following basic cadmium compounds form white crystalline precipitates: the *sulphate* has the formula  $2\text{CdO}, \text{SO}_3 + \text{H}_2\text{O}$ ; the *nitrate*,  $12\text{CdO}, \text{N}_2\text{O}_5 + 11\text{H}_2\text{O}$ ; the *chloride*,  $\text{CdCl}_2, \text{CdO} + \text{H}_2\text{O}$ .

P. P. B.

**Hydrates of Chromic Chloride.** By L. GODEFROY (*Compt. rend.*, 100, 105—108).—A mixture of 7 parts ethyl alcohol with 3 parts potassium dichromate is saturated with chlorine gas (Abstr., 1884, 1266), the solution filtered through cotton-wool, and the filtrate distilled until it separates into two layers. On cooling, the green lower layer solidifies to a mass of crystals which are purified by recrystallisation from a small quantity of water. The crystals thus obtained are thin lozenge-shaped lamellæ which readily give off some of their water, but can be preserved in a closed vessel. They have the composition  $\text{Cr}_2\text{Cl}_6 + 12\text{H}_2\text{O}$ .

The hydrate,  $\text{Cr}_2\text{Cl}_6 + 20\text{H}_2\text{O}$ , is obtained by placing a saturated solution of the preceding salt in a dry vacuum for several days at a temperature below  $+6^\circ$ . It forms brilliant green triclinic needles as much as 3 cm. in length. These crystals readily give off some of their water; above  $6^\circ$  or  $7^\circ$  they melt slowly in their water of crystallisation. When placed over sulphuric acid, the crystals lose  $8\text{H}_2\text{O}$  and become opaque and friable.

The hydrate,  $\text{Cr}_2\text{Cl}_6 + 8\text{H}_2\text{O}$ , is a pale-green powder obtained by keeping the duodecahydrate in a dry vacuum until it ceases to lose weight.

All these hydrates are extremely soluble in water, and they also dissolve readily in alcohol or ethyl acetate, forming green solutions which show no dichroism. That they are true hydrates of chromic chloride, and not oxychlorides or hydrochlorides of chromic oxide is shown by the fact that they readily form double chlorides with alkaline chlorides.

Dilute aqueous solutions of these salts slowly become bluish-violet in colour at the ordinary temperature, and the change is instantaneous at about  $70$ — $80^\circ$ . Concentrated solutions do not alter in this way, even after prolonged boiling. It seems probable that the chromic chloride is converted into an oxychloride with liberation of hydrochloric acid, and that decomposition ceases when a certain quantity of hydrochloric acid has been set free. This supposition is supported by the fact that the change is entirely prevented by the presence of 2.5 per cent. of free hydrochloric acid.

C. H. B.

**Purple of Cassius.** By M. MÜLLER (*J. pr. Chem.* [2], 30, 252—279).—Numerous methods have been described for the preparation of this colour, in which the presence of both stannic and stannous chlo-

rides appears to be essential: the results, however, are very uncertain, and the varying composition and appearance of the products obtained have led to widely differing views as to the constitution of this purple. It has long been a disputed point as to whether the gold is present as metal or suboxide. Acting on the supposition that the former view was correct, the author concluded that the finely divided metallic gold might give colour to other substances besides stannic oxide, and he therefore tried experiments with the object of confirming this view. Magnesium oxide in fine pulp was mixed with a solution of gold chloride: the resulting mixture of magnesia and gold oxide was washed free from chloride, dried, and ignited in a platinum crucible. A beautiful intensely purple powder was the result, perfectly homogeneous and surpassing in brilliancy any of the tin purples. By varying the quantity of gold all shades from a pale rose to a deep carmine tint can be obtained, 0.1 per cent. of gold being sufficient to colour the magnesium oxide pink. In this case, the colour is obviously due to finely divided metallic gold, as similar results are obtained by igniting the mixture in a stream of hydrogen, and the purple colour is destroyed by igniting at a temperature sufficiently high to melt gold.

Similar results were obtained by using lime instead of magnesia, but the lime required much more gold to give the same tint as that obtained in the magnesia purples.

Endeavours were next made to colour barium sulphate by suspending the latter in gold chloride solution, and reducing the gold by various reagents, drying and igniting the resulting product. It was found that barium sulphate could thus be easily made to yield purples of various degrees of intensity, although not equal to those obtained from magnesia. Reduction of the gold solution with grape-sugar gave the best results. Purples of this kind were also obtained with calcium carbonate and phosphate, but an unsatisfactory result was obtained with silica. Zinc and lead oxides also yielded purples with gold chloride. The best result of all was, however, produced by alumina: this purple is many times more intense in colour than the magnesia purple, and was prepared at first in the same way, the starting point being the precipitated hydrate: as however by this process the whole of the gold cannot be removed from solution, it is best as in the case of barium sulphate to reduce the gold by means of an alkaline solution of grape-sugar: the solution is kept in constant motion and heated up to a point at which the colour is a bright scarlet: if the operation is not stopped at this point a brownish-red is obtained, which on drying and igniting yields a purple of no brilliancy. Stannic oxide treated in this way also yields fine purples: the best proportions for obtaining a 10 per cent. stannic oxide purple are as follows:—A quantity of stannic chloride equivalent to 9 grams  $\text{SnO}_2$  is dissolved in 200 c.c. of water, potassium carbonate added to alkaline reaction, then 1 gram of gold as chloride, and the grape-sugar added, and the whole diluted to 300 litres and warmed until the colour has assumed its most brilliant tone. The stannic oxide purples are at their best inferior to magnesia or alumina purples.

The author finds that an alkaline solution of glycerol is an excellent reagent for reducing gold: the reduction takes place at the ordinary

temperature, and the gold is deposited in an exceedingly fine state of division. The above experiments show that gold is able to colour not only stannic oxide, but a large number of other bodies of various chemical constitution, whether bases, acids, or salts. The colour cannot therefore be due to any chemical combination, but simply to the presence of finely divided metallic gold.

J. K. C.

**Atomic Weight of Bismuth.** By R. SCHNEIDER (*J. pr. Chem.* [2], **30**, 237—251).—Lagerhjelm's determination of the atomic weight of bismuth, which up to 1851 was accepted as correct, was based on the conversion of the metal into (1) sulphide; (2) oxide; and (3) sulphate: the second of these methods he considered the most trustworthy, and from five experiments the number 213 was deduced as the atomic weight of bismuth. Following a remark of Gmelin's, the author in 1851 revised Lagerhjelm's experiments, selecting the conversion of metal into oxide as the safest method, and as a mean of eight determinations found the atomic weight to be 208 ( $O = 16$ ). In 1859, however, Dumas by estimating the amount of chlorine in bismuth chloride, calculated that the atomic weight of bismuth was 210. That this number is too high follows from several considerations. Dumas himself acknowledged the difficulty of rendering soluble the whole of the chlorine present by means of soda solution as, after repeated treatment with the latter reagent, small quantities of chlorine were still left in the insoluble residue. The strongly hygroscopic character of bismuth chloride renders it also unsuitable for atomic-weight determinations: the least contact with the atmosphere causes it to absorb moisture, so that on distillation small quantities of oxychloride are formed which are very difficult to get rid of, and by lowering the percentage of chlorine give a number for the atomic weight of bismuth which is too high; the same error was found by Cooke to have vitiated Dumas' estimation of the atomic weight of antimony.

Marignac has lately made a fresh investigation of this question. By the reduction of bismuth trioxide in a stream of hydrogen, he obtained the number 208·6, but considered this as rather too high, because a small quantity of suboxide was formed which could not be entirely reduced to metal. By the conversion of the oxide into sulphate he obtained as the mean of six experiments 208·16 as the atomic weight of bismuth, a number which agrees very closely with that obtained by the author. This number has also been lately confirmed by Löwe.

J. K. C.

**Nitric Peroxide in Bismuth Subnitrate.** By HAGER (*Arch. Pharm.* [3], **22**, 741, and *Pharm. Centr.*, **32**).—Bismuth subnitrate often has the odour of nitric peroxide. Hager explains the formation of this impurity as follows:—Free nitric acid under the influence of sunlight decomposes into oxygen and nitric peroxide. If light and air be not carefully excluded from moist bismuth subnitrate, a little nitric acid becomes free and is decomposed as above. To prevent this decomposition, the subnitrate should be preserved from light and air in well-stoppered glass vessels. To renovate such subnitrate, it is placed in thin layers on porcelain and heated at 30—35° for not more than 20 minutes.

J. T.

**Atomic Weight of Platinum.** By W. HALBERSTADT (*Ber.*, 17, 2962—2975).—The author has made a series of careful determinations of the atomic weight of platinum. The compounds employed were platinic bromide, and potassium and ammonium platinochlorides and platinobromides. The estimations of the platinum were carried out by Seubert's method of the reduction of the salt in a current of hydrogen, and also by Classen's method of electrolytic deposition. The author also attempted to employ the estimation of the chlorine and bromine by the various methods in use, but abandoned this attempt as these methods did not prove accurate enough for an investigation of this kind. In the analysis of the potassium platinochloride, the potassium chloride or bromide was also estimated. 300 grams of platinum were employed in the investigation, and this was carefully purified by the Bunsen-Schneider process. The platinic bromide was prepared by the method of v. Meyer and H. Züblin (*Abstr.*, 1880, 445). During the preparation, the author obtained *hydrogen platinobromide* in the form of monoclinic crystals easily soluble in water, alcohol, ether, chloroform, and glacial acetic acid, insoluble in carbon disulphide. *Platinic bromide* was not obtained in a crystalline condition, but formed a dark brown non-hygroscopic powder sparingly soluble in water; 100 grams of an aqueous solution saturated at 20° contained 0.41 gram  $\text{PtBr}_4$ . The *ammonium platinobromide* was obtained by the addition of the calculated quantity of ammonium bromide to a dilute aqueous solution of hydrogen platinobromide or to an aqueous solution of platinic bromide. It forms small carmine-red octahedra. 100 grams of an aqueous solution saturated at 20° contain 0.59 gram of the dry salt. The *potassium platinobromide* employed was prepared in exactly similar ways and crystallised in red octahedra: 100 grams of an aqueous solution saturated at 20° contained 2.02 grams of the dry salt.

Altogether 97 determinations of the atomic weight were made: namely, 10 with platinic bromide, 32 with ammonium platinobromide, 18 with potassium platinobromide, 18 with ammonium platinochloride, and 19 with potassium platinochloride. The results obtained were as follows:—By decomposition by ignition in a current of hydrogen, the atomic weight deduced from 59 platinum estimations = 194.54246; from the ratio  $\text{KBr}$  or  $\text{KCl} : \text{Pt}$  (18 estimations) = 194.77061; by decomposition by electrolysis, the atomic weight deduced from 38 platinum estimations = 194.36073; and from the ratio  $\text{KBr}$  or  $\text{KCl} : \text{Pt}$  (19 estimations) = 194.62987.

The mean of all the results obtained gives the atomic weight of platinum as 194.57592, which agrees very closely with the number 194.46 found by Seubert (*Abstr.*, 1881, 514). L. T. T.

**New Rhodium Salt.** By WILM (*Bull. Soc. Chim.*, 42, 327).—In the preparation of the salts described by Claus ( $\text{Rh}_2\text{Cl}_6, \text{NH}_4\text{Cl} + 3\text{H}_2\text{O}$  and  $\text{Rh}_2\text{Cl}_6, 3\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$ ), in presence of excess of aqua regia, the compound  $\text{Rh}_2\text{Cl}_6, 8\text{NH}_4\text{Cl} + 7\text{H}_2\text{O}$  is precipitated in crimson hexahedral plates. It is decomposed by water, yielding one or other of the former salts. After all the rhodium has been precipitated, the mother-liquor still contains a substance which often accom-

panies rhodium, and is probably the cause of anomalies in the reaction of rhodium salts.

W. R. D.

**New Compounds of Iridium.** By C. VINCENT (*Compt. rend.*, 100, 112—114).—When moderately concentrated and boiling solutions of iridium tetrachloride and mono-, di-, or tri-methylamine hydrochloride are mixed, and the liquid allowed to cool, double chlorides separate in crystals, and can easily be purified by recrystallisation. These iridiochlorides have the general formula  $\text{IrCl}_4 \cdot 2\text{AmCl}$ , where  $\text{Am}$  stands for the amine.

*Monomethylamine iridiochloride* forms small hexagonal tables of a very dark reddish-brown colour.

*Dimethylamine iridiochloride* crystallises in rhombic octahedra of a rich reddish-brown colour. The crystals cleave parallel with the face  $m$ , and the ratio of the axes  $D : d : h = 1.9689 : 1 : 1.9540$ .

*Trimethylamine iridiochloride* forms large reddish-brown regular octahedra. The ease with which this compound crystallises may be used as a means of separating iridium from the traces of rhodium which it frequently retains.

All three compounds are decomposed by heat with intumescence, and a residue of iridium and carbon is left. The carbon burns rapidly when heated in the air, and leaves a bulky very brilliant residue of perfectly pure iridium.

C. H. B.

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### Mineralogical Chemistry.

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**Occurrence of Gold in Brazil.** By O. A. DERBY (*Amer. J. Sci.* [3], 28, 440—447).—Two peculiar modes of occurrence of gold are described. A specimen in the National Museum at Rio de Janeiro, from Ponte Grande, Sabará, province of Minas Geraes, shows films of gold resting on the surface of a secondary mineral, limonite; the conditions are such that, the author thinks, they cannot be accounted for except on the hypothesis of natural deposition from solution. The districts of Campanha and São Gonçalo, in southern Minas Geraes, afford an example of extensive auriferous deposits in decomposed gneiss, in which the almost complete absence of veins and of the other usual concomitants of gold is remarkable.

B. H. B.

**Ozokerite.** By F. S. SMITH (*Chem. News*, 51, 35).—A combustion of an unpurified sample of ozokerite found in some clay fields in South Amboy, New Jersey, gave the following figures per cent. :—C, 86.46; H, 12.83. The hydrocarbons probably belong to the  $C_nH_{2n}$  series.

D. A. L.

**Genesis of the Specular Iron Ores of Cuba.** By J. P. KIMBALL (*Amer. J. Sci.* [3], 28, 416—429).—The Juragua hills are the culmination of the foot-hills of the Sierra Maestra, between the bays of Santiago and Guantanamo. They are distinguished from the

massive body of the Sierra by their isolation as four distinct ranges. The second range affords the best type of ore bodies. The diorite of these hills is in contact with the syenite, and the contact seems to have become the seat of great chemical activity. The large masses of iron ore are secondary products from the decomposition of basic eruptive rock, now represented by the epidotic diorite that has penetrated the syenite of the Sierra Maestra. The best of the iron ore bodies are replacements of coralline limestone. Proof of this replacement is afforded by fragments of the ore still retaining the structure of coral. Collateral proof is to be found in the presence of isolated masses of marble without stratification, but with marked prismatic cleavage.

The larger ore bodies present all the numerous physical types of specular oxide, besides a variety of phases from unequal distribution of iron pyrites and of magnetic and manganic oxides, and from an unequal degree of hydration. Earthy admixtures are of a chloritic and epidotic type, and thus essentially basic. The composition of the ore is shown by the following percentages from commercial samplings:—Moisture, 0·24 to 0·81; silica and insoluble, 5 to 10·5; phosphorus, 0·009 to 0·065; sulphur, 0·045 to 0·248; and iron, 61 to 68·5.

Besides the iron ore bodies, above described as *replacements*, another class of deposits of ferric oxide are described as *concentrations*. These are partially altered dioritic masses characterised by a notable but unequal concentration of ferric oxide *in situ*. The outcropping portions of such masses are often no less rich in specular oxide than the replacements of coralline, from which they are readily distinguished by their superior hardness and density, as well as by their metasomatic association with unaltered diorite.

B. H. B.

**Bauxite from Langsdorf.** By J. LANG (*Ber.*, 17, 2892—2894). The bauxite found in this neighbourhood varies considerably in colour (from bright red to brownish-red), chemical composition, density, &c. The following are the results of the analysis of two specimens. (I.) Brownish-red specimen. (II.) Light red specimen.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
I.	5·14	50·85	14·36	0·35	0·41	0·11	0·09	0·17
II.	10·27	49·02	12·90	—	0·62	trace	0·11	0·20

	H <sub>2</sub> O. at 100°.	H <sub>2</sub> O. on ignition.	CO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	Total.
I.	1·35	27·03	trace	0·48	100·34
II.	0·93	25·88	0·26	0·38	100·57

A microscopic examination showed the presence of crystals of magnetic iron-ore, augite, silicic acid, and silicates, and of amorphous red hæmatite, and (probably) aluminium hydroxide. From the analyses and mineralogical character of this substance, the author considers it to be a product of the weathering of basalt.

L. T. T.



**Hemihedrism of Cuprite.** By H. A. MIERS (*Phil. Mag.* [5], **18**, 127—130).—Among certain specimens of cuprite from Wheal Phcenix, Cornwall, a mode of hemihedrism was observed whose existence has been considered possible on theoretical grounds, but has only been previously observed in ammonium chloride. This mode, described as the trapezohedral or gyroidal, is formed by the combination of the cube, octahedron, and dodecahedron. The following were the observations of the angles:—

(100) :  $\alpha = 47^\circ 30'$  [18 edges]; (010) :  $\alpha = 53^\circ 43'$  [18 edges]; (001) :  $\alpha = 63^\circ 58'$  [18 edges]; (111) :  $\alpha = 9^\circ 23'$  [11 edges].

If the alternate faces of the complete 48-faced figure be suppressed, two half forms are obtained, for which the cube and dodecahedral planes are no longer symmetrical; such two half forms are exantromorphous.

V. H. V.

**Erosion of Limestone.** By A. L. EWING (*Amer. J. Sci.* [3], **29**, 29—31).—In attempting to determine the amount and rate of chemical erosion taking place in the Limestone Valley of Center Co., Pennsylvania, the nature of the problem precludes the idea of even a close approximation to accuracy. The author claims, however, that his determinations form a more trustworthy basis than mere estimates. The method pursued was as follows:—The amount of water flowing from a given hydrographic basin in the region under question was determined from the cross section and velocity of the stream draining it. The amount of solids in the water was determined by evaporation. These data, with the area of the basin, formed the basis of calculation.

The region selected was that of the Spring basin, which forms a considerable portion of the limestone valley of Center Co. The author's calculations show that 25,456,560 kilos. of solids are removed per annum. As the limestone area drained by Spring Creek is about 100 square miles, this gives 255,654 kilos. of solids as the amount removed per annum per square mile. This is equivalent to 282 tons. Making a correction for the water carried off by Spring Creek, which falls upon the mountains bordering the valley, it still leaves 275 tons per square mile as the amount annually removed in solution.

B. H. B.

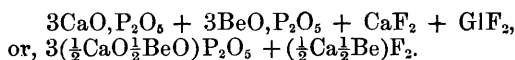
**Colemanite.** By A. W. JACKSON (*Amer. J. Sci.* [3], **28**, 447—448; comp. this vol., p. 224).—This mineral has recently been determined by J. T. EVANS, whose analysis gives the formula  $2\text{CaO}, 3\text{B}_2\text{O}_3 + 5\text{H}_2\text{O}$ . It differs from pandermite in containing 5 mols. instead of 3 mols. of water, but its main interest lies in its morphological relations. The crystals are small and colourless; the examination in the polariscope showed them to be monoclinic. The plane of the optic axis is normal to the clinopinacoid, and makes an angle of  $83^\circ 25'$  with the chief axes. With a primitive form having  $a : b : c = 0.774843 : 1 : 0.540998$ , and  $\beta = 69^\circ 50' 45''$ , the author determined the following forms:  $\infty\text{P}\infty$ ,  $\infty\text{P}\infty$ ,  $0\text{P}$ ,  $\infty\text{P}^3$ ,  $\infty\text{P}^{\frac{1}{2}}$ ,  $\infty\text{P}^{\frac{1}{3}}$ ,  $\infty\text{P}^{\frac{1}{6}}$ ,  $\infty\text{P}$ ,  $\infty\text{P}^2$ ,  $\text{P}\infty$ ,  $2\text{P}\infty$ ,  $\frac{4}{11}\text{P}\infty$ ,  $6\text{P}\infty$ ,  $4\text{P}\infty$ ,  $2\text{P}\infty$ ,  $\text{P}\infty$ ,  $-\text{P}\infty$ ,  $\text{P}$ ,  $2\text{P}$ ,  $-\text{P}$ ,  $-3\text{P}$ ,  $-\frac{1}{2}\text{P}$ ,  $2\text{P}^2$ ,  $3\text{P}^{\frac{1}{2}}$ ,  $4\text{P}^2$ ,  $\frac{3}{2}\text{P}^{\frac{1}{2}}$ ,  $2\text{P}^2$ ,  $3\text{P}^2$ ,  $-3\text{P}^2$ ,  $3\text{P}^3$ ,  $4\text{P}^4$ ,  $-3\text{P}^3$ . The crystals are all very complex. One of them has 24 different forms upon it.

The primitive prism  $\infty P$  is always largely developed, and determines the columnar habit of the crystals. B. H. B.

**Herderite from Oxford Co., Maine.** By W. E. HIDDEN and J. B. MACKINTOSH (*Amer. J. Sci.* [3], 27, 135—138).—The specimens of the mineral described were originally thought to be topaz, but the authors noticed that the basal cleavage was absent, and that the hardness was 5 instead of 8. The crystals are implanted on quartz or on muscovite, and have an average diameter of about 3 mm. They are apparently rhombic, well-formed, and rich in planes. Streak white. Crystals very brittle with conchoidal fracture. Sp. gr. = 3. Phosphoric anhydride was found to be present in large quantity. These results prove that the mineral is herderite, or a new mineral species. As no quantitative analysis of herderite has ever been published, the authors made an analysis in order to determine its formula. The results obtained were as follows:—

CaO.	BeO.	P <sub>2</sub> O <sub>5</sub> .	F.	Total.	Less O.	Total.
33.21	15.76	44.31	11.32	104.60	4.76	99.84

Corresponding with the formula—



These results are interesting, since it is the first time that beryllium has been found in any mineral in any other form than as a silicate or aluminate. The mineral is probably identical with the herderite of Haidinger, described as an *alumina* lime phosphate fluoride. Should it prove otherwise, the authors suggest the name of *glucinite* as appropriate (comp. Abstr., 1884, 827, and 1102). B. H. B.

**Saltpetre Deposit.** By SACC (*Bied. Centr.*, 1884, 784—785).—Near Anané, in Bolivia, a deposit occurs having the composition: potassium nitrate 60.7; sodium chloride and water 30.7; organic matter 8.6 per cent. with traces of borax. The soil under the deposit is brown, and when moistened an odour of ammonium carbonate and sulphhydrate is noticed; the analyses show its composition to be:—residue after ignition (sand, calcium, magnesium, and iron phosphates) 74.2 per cent.; borax and salts 15.5; organic matter, water, and ammonium salts 10.3. The author thinks that the nitrate has been formed by the oxidation of the ammonium salts in presence of the sodium and potassium derived from the underlying shale. The potassium nitrate has risen by capillarity to the surface, whilst the more deliquescent sodium nitrate has been washed away to the hotter and drier regions of the coast, there forming Chili saltpetre deposits. As many fossil bones are found here, it is possible that these saltpetre deposits are all due to the decomposition of the remains of antediluvian animals.

E. W. P.

**A New Tantalite Locality.** By C. A. SCHAEFFER (*Amer. J. Sci.* [3], 28, 430).—At the Etta tin mine, Dakota, crystals occur of a black mineral, believed by Blake (*Amer. J. Sci.* [3], 26, 235) to be wolframite. A careful examination of all the specimens received by

the author has resulted in finding no wolframite, but a considerable quantity of tantalite, which gave on analysis the following results:—

Ta <sub>2</sub> O <sub>5</sub> .	SnO <sub>2</sub> .	FeO.	MnO.	Total.	Sp. gr.
79·01	0·39	8·33	12·13	99·86	7·72

B. H. B.

**Columbite in the Black Hills of Dakota.** By W. P. BLAKE (*Amer. J. Sci.* [3], 28, 340—341).—At the Etta and Ingersoll mines, Dakota, columbite associated with cassiterite, albite, and mica occurs in granite dykes traversing the mica schists and sandstones. At the Ingersoll mine, an enormous mass of nearly pure columbite with inclusions of quartz was found protruding from a matrix of albite and quartz. The mass weighed about one ton. Thin tabular crystals occurred at the lower end, where it was enclosed in quartz. The habit of the Ingersoll crystals is thin and tabular, with acute, wedge-like prismatic edges, the plane  $\infty P\bar{2}$  being nearly obliterated by the extension of  $\infty P\bar{3}$  and  $\infty P$ ; whilst at the Etta mine the seplanes are subordinate to  $\infty P\bar{2}$  and  $\infty P\bar{2}$ . The plane  $0P$  is narrow in the crystals from both localities, and is flanked by a series of bevelling planes,  $\frac{1}{2}P\bar{2}$  being especially prominent.

Several cavities in the large mass were filled with a yellow powder, consisting chiefly of hydrous uranium oxide.

The blowpipe reactions of the Ingersoll columbite are peculiar in the amount of manganese indicated.

B. H. B.

**Sand and Kaolin from Quartzite.** By J. D. DANA (*Amer. J. Sci.* [3], 28, 448—452; 29, 57—58). From observations made (*Amer. J. Sci.* [3], 28, 203) on the quartzose rocks of Minas Geraes, Brazil, O. A. Derby inferred that the flexibility attributed to them is not an original characteristic, but only a surface character, a phase of weathering or decay brought about by percolating waters. Facts from the quartzite regions of Massachusetts, Connecticut, and Vermont fully sustain these observations, and appear to throw light on the nature of the change. The conclusion from the facts described by the author is, that the kaolin is derived from the felspar of a felspathic quartzite. The quartzite contained much felspar, and only traces of iron pyrites and mica, and was easily permeable by water, hence its fitness for making deposits of pure white clay. It is also evident that the quartz, sand, and friable part of the quartzite are produced by the removal of finely disseminated felspar; whilst the buhrstones have been found where the felspar is disseminated in largish pieces through the quartzite. A very common source of the destruction of the quartzite is the oxidation of its iron pyrites. One peculiar result of this oxidation is a pseudo-breccia; this is a quartzite divided up by a succession of cracks, with limonite colouring the rock alongside of the cracks, and also deposited in them. Within some of the dark limonite-coloured bands, cavities occur containing a coating of limonite. They have generally a lining of minute quartz crystals coating the limonite, showing that the quartz was deposited after the limonite. The quartz penetrates the limonite-coloured bands to such an extent that it is probable that they were also

produced during the formation of the limonite, and at the ordinary temperature.

The only fact as yet observed which seems to bear on the origin of these evidently recent quartz deposits, is that the quartzite mass shows by the occurrence in it of a few large ragged cavities, and also of many minute holes, that the rock probably contained grains and larger pieces of felspar. If so, alkaline silicated solutions, derived from the action of carbonated waters on the felspar, may have been the source of the crystals. This supposition is reasonable, but more facts are needed to sustain it.

B. H. B.

**Siliceous Earth from Morris Co., New Jersey.** By J. W. MCKELVEY (*Chem. News*, 51, 35).—This sample of infusorial earth was greyish-white in colour, and on ignition becomes perfectly white. It contains small fragments of leaves and twigs. Its density is 1.11; on analysis it gave, per cent.:  $\text{SiO}_2$ , 80.66;  $\text{Al}_2\text{O}_3$ , 3.84;  $\text{CaO}$ , 0.58; loss on ignition, 14.01. The deposit from which it was obtained is 3 acres in extent. It is peaty for 1 foot from surface, then infusorial earth for 3 feet, followed by 7 feet of white clay, resting on a drift of gravel and cobble-stone. The clay is mixed throughout with infusorial earth. The deposit is thin near the edges, and the upper 15 inches of the 3-foot layer is more porous than the rest.

D. A. L.

**Chrysotile from Shipton, Canada.** By E. G. SMITH (*Amer. J. Sci.* [3], 29, 32—33).—The fibrous serpentine, or chrysotile from Shipton occurs in narrow veins traversing the solid serpentine. The mineral has a fine silky lustre, and varies in colour from deep green to pale yellow. Two specimens were analysed: I, dark green, sp. gr. 2.142; II, pale yellow, density 2.286. The results were as follows:—

	$\text{SiO}_2$ .	$\text{FeO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ .	Total.
I.	41.837	2.234	41.990	14.282	100.343
II.	42.043	3.663	39.540	14.309	99.555

These results clearly establish the identity of this mineral with the chrysotile from other localities.

B. H. B.

**Nephrite from Jordansmühl in Silesia.** By H. TRAUBE (*Jahrb. f. Min., Beilage* iii, 412—427).—Nephrite has recently been found *in situ*, with granulite and serpentine at Jordansmühl. The structure and colour of the nephrite are extremely variable. The colour is, as a rule, a dark-green; the compact varieties have mostly a fine olive-green colour and great transparency. The nephrite encloses magnetite, compact epidote, and zoisite. The chemical composition is tolerably uniform, the differences being confined to the percentage of iron. The Jordansmühl nephrite differs in microscopic structure from all other occurrences, and proves Arzruni's theory, that every occurrence of nephrite has a special microscopic structure. If the composition, manner of formation, and geological occurrence are regarded apart from the structure, two varieties of the Jordansmühl nephrite may be

assumed; the pyroxene-nephrite, (Analysis I) closely connected with the granulite, and the primary nephrite (Analysis II) occurring in the serpentine.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.
I.	56·93	1·01	4·99	0·71	14·54	19·21
II.	59·21	1·16	2·40	0·80	14·08	20·81
	H <sub>2</sub> O.		Total.		Density.	
I.	1·93		99·32		2·982	
II.	1·81		100·27		3·043	

B. H. B.

**The Santa Catharina Meteorite.** By O. A. DERBY (*Amer. J. Sci.* [3], 29, 33—35).—An ochreous crust is mentioned by Daubrée as occurring on some of the specimens of the Santa Catharina meteorite now in the National Museum of Rio de Janeiro. This crust he took to be of secondary or terrestrial origin, and to be composed of limonite with imprisoned fragments of the disintegrated granite upon which the mass was stated to have rested. This crust, however, proves to be an essential part of the meteorite, and appears to indicate the existence of a new group of meteorites intermediate between the holosiderites and the syssiderites of Daubrée. The meteorite presents a mixture of metallic and siliceous elements combined in a way that has not hitherto been noticed, and the stony portion also presents a new type of structure in which olivine and plagioclase predominate. The partial vitrification of the stony portions affords evidence of the meteoric origin of the mass. The author is collecting material for a more extended memoir.

B. H. B.

**Mineral Spring "Römerbrunnen" at Echzell Wetterau.** By C. PISTOR (*Ber.*, 17, 2894—2896).—This spring rises, at an elevation of 450 feet above the level of the North Sea, on the western slope of the Vogelsgebirg, in a stratum of peat (1·75 feet thick), overlying late diluvial deposits. Analysis of the water yielded the following results in parts per 1000:—

SiO <sub>2</sub> .	CO <sub>2</sub> .	N <sub>2</sub> O <sub>6</sub> .	N <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeCO <sub>3</sub> .	MgCO <sub>3</sub> .
0·090	2·7910	trace	trace	0·0450	0·0205	0·5611
CaCO <sub>3</sub> .	CaSO <sub>4</sub> .	NaCl.	KCl.	MgCl <sub>2</sub> .	Organic matter.	NH <sub>3</sub> .
1·0590	0·1240	1·6275	0·0642	0·1780	0·0230	trace

The temperature of the water issuing from the spring was 12·3°.

L. T. T.

## Organic Chemistry.

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### Reactions of Aluminium Salts with Organic Compounds.

By GUSTAVSON (*Bull. Soc. Chim.*, **42**, 325—327).—The reactions of haloïd aluminium salts with organic compounds may be divided into two classes, the first, in which combination occurs, and the second, where double decomposition is effected. To this latter class belong those reactions where, by means of the corresponding haloïd salt of aluminium, the chlorine or bromine of certain simple compounds, ( $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_6$ , &c.), which do not contain oxygen, is replaced by another halogen. If the organic compound contains hydrogen in addition to the halogen, a halogen hydride is evolved, while the elements that remain form an unsaturated radical which at once combines with the aluminium salt, unless some indifferent liquid is added in the first place, when substitution of the halogen takes place. In those reactions where combination occurs, either the aluminium salt combines directly with the organic compound, or decomposition is in the first place effected, resulting in the formation of an unsaturated radical, which then combines with the aluminium salt. The compounds studied by the author contained either hydrocarbon radicals or oxygen in addition to carbon and hydrogen. As instances of the first set of compounds, benzenoid hydrocarbons and olefines may be taken; these combine directly with haloïd aluminium salts, provided a halogen hydride be present. The compounds formed enter into reaction with other substances with great facility. Ethylene combines with aluminium bromide, producing a compound of the formula  $\text{Al}_2\text{Br}_6\text{C}_2\text{H}_4$ , and similar reactions occur with saturated hydrocarbons, whilst at the same time simpler saturated hydrocarbons are formed. The organic radicle which remains conjugated with the aluminium salt combines with other substances, and, in fact, appears to act in precisely a similar manner to the free aluminium salt. The reactions of haloïd aluminium salts with the chlorides and bromides of the saturated alcohols resemble those with the saturated hydrocarbons. These salts also combine with compounds which contain oxygen. Thus aluminium chloride combines with sulphurous anhydride and also with compound ethers. In these cases, saturated compounds are decomposed, forming an unsaturated radical, which combines with the aluminium salt. For instance, the chlorides of the fatty acids, when acted on by aluminium chloride, evolve hydrogen chloride and an unsaturated radical containing oxygen is produced, and remains combined with the aluminium chloride,  $\text{Al}_2\text{Cl}_6 + 4\text{C}_2\text{H}_5\text{OCl} = 4\text{HCl} + \text{Al}_2\text{Cl}_6\text{C}_8\text{H}_8\text{O}_4$ . The author considers that mineral salts perform an important function in the living organism by combining with organic matter to form unstable compounds, which readily enter into reaction with other bodies, and enable the organism to harmonise with changes in the environment.

W. R. D.

**Chloroform Hydrate.** By G. CHANCEL and F. PARMENTIER (*Compt. rend.*, **100**, 27—30).—If a mixture of chloroform and water

is cooled at  $0^{\circ}$  with frequent agitation, the hydrate,  $\text{CHCl}_3 \cdot 18\text{H}_2\text{O}$ , separates in colourless lamellæ resembling crystals of potassium chlorate. The crystals are lighter than chloroform but heavier than its aqueous solution. They melt at  $1.6^{\circ}$ , and form a milky liquid which soon separates into chloroform and water.

Sometimes the hydrate will not crystallise unless some previously formed crystals are dropped into the cooled mixture of chloroform and water. If the mixture is cooled below  $0^{\circ}$  with frequent agitation, the crystals which separate are not chloroform hydrate, but ice mixed with very small proportions of chloroform. This result is due to the fact that the heat of formation of chloroform hydrate is less than the latent heat of water. The heat of formation of the hydrate from liquid water and liquid chloroform is  $22.9$  cal., and is the same as its heat of fusion, but its heat of formation from ice and solid chloroform is negative, and combination would therefore be endothermic.

The amount of chloroform in the hydrate was determined by heating it with aqueous or alcoholic potash in sealed tubes at  $100^{\circ}$ , and precipitating the chlorine as silver chloride. C. H. B.

**Constitution of Nitroparaffins.** By KIESEL (*Bull. Soc. Chim.*, **42**, 319).—When the nitroparaffins are prepared by the action of silver nitrite on iodo-derivatives, secondary products are formed; these have been examined by the author. They appear to be isomerides of the nitroparaffins and alcoholic nitrites. In the cases of nitroethane and nitropropane, compounds are formed which boil at  $29.5^{\circ}$  and  $55^{\circ}$  respectively. When the latter compound is treated with hydrogen chloride, ammonium chloride is formed, together with a crystalline substance, which, from its chemical behaviour, appears to be the hydrochloride of a base,  $(\text{CHO})_2\text{C}:\text{NH}, \text{HCl}$ . The nitrate of this base was also prepared. A similar compound is formed by the action of hydrogen chloride on the new isomeride of nitromethane, but was not obtained pure. W. R. D.

**Alkaline Ferrocyanides and their Compounds with Ammonium Chloride.** By A. ÉTARD and G. BÉMONT (*Compt. rend.*, **100**, 108—110; see also this vol., p. 233).—When dry potassium ferrocyanide is heated to incipient fusion in a vacuum, no gas is evolved, but a part of the salt is converted into potassium cyanide, which can be dissolved out by alcohol, and Williamson's salt, which is left in somewhat bulky crystals,  $2\text{K}_4\text{FeCy}_6 = \text{FeK}_2\text{FeCy}_6 + 6\text{KCy}$ .

The ferrous potassium salt decomposes at a red heat into potassium cyanide, cyanogen, and pure crystalline iron; thus,  $\text{FeK}_2\text{FeCy}_6 = \text{Fe}_2 + 2\text{KCy} + 2\text{CN}$ . The complete decomposition of the potassium ferrocyanide is represented by the equation  $\text{K}_4\text{FeCy}_6 = \text{Fe} + 4\text{KCy} + 2\text{CN}$ .

If a solution of potassium ferrocyanide is allowed to drop into a solution of ammonium chloride, boiling out of contact with the air, decomposition takes place in accordance with the equation  $2\text{KFeCy}_6 + 6\text{NH}_4\text{Cl} = \text{FeK}_2\text{FeCy}_6 + 6\text{NH}_4\text{Cy} + 6\text{KCl}$ . When equal bulks of granular ammonium chloride and potassium ferrocyanide are treated with twice their volume of water at  $25^{\circ}$ , with frequent agitation, a

crystalline mass is formed, and if this is dried by means of a filter-pump and redissolved in water at 35–40°, the solution on cooling deposits large, brilliant, refractive, yellowish crystals of the composition  $(\text{NH}_4)_3\text{KFeCy}_6, 2\text{NH}_4\text{Cl}$ . When equal parts of potassium ferrocyanide and ammonium chloride are dissolved at 100°, the solution on cooling deposits ammonium chloride and pale yellow rhombohedra of the composition  $\text{NH}_4\text{KH}_2\text{FeCy}_6, 2\text{NH}_4\text{Cl}$ . Ammonium ferrocyanide can only be obtained by saturating hydroferrocyanic acid with ammonia and precipitating with alcohol. When dissolved, it decomposes, yielding, amongst other products, ammonium cyanide. If ammonium ferrocyanide, or better, sodium ferrocyanide, is treated with ammonium chloride, Bunsen's salt,  $(\text{NH}_4)_4\text{FeCy}_6, 2\text{NH}_4\text{Cl}$ , is obtained. This salt splits up into ammonium cyanide and ferrous chloride, a reaction which shows that the iron in ferrocyanides has a ferrous function.

C. H. B.

**Action of Chlorine on Ethyl Thiocyanate.** By J. W. JAMES (*J. pr. Chem.*, **30** [2], 316–317).—When chlorine is passed through cooled ethyl thiocyanate, crystals of cyanuric chloride separate, and a liquid is formed which boils between 130–140° with partial decomposition, and consists of dichlorethyl sulphochloride.

J. K. C.

**Preparation of Canarine.** By MILLER (*Bull. Soc. Chim.*, **42**, 328).—The author recommends the following process for the preparation of canarine. One part of potassium thiocyanate is dissolved in two parts of water, and to this liquid is added one-tenth part of Berthollet's salt and one part of hydrochloric acid. The reaction commences at once, and after it has subsided, the vessel is cooled by water, and one-tenth part of Berthollet's salt and one part of hydrochloric acid are again added. The temperature should not be allowed to fall below 80°. The crude canarine is washed with water and purified by dissolving it in potash, from which solution the potassium derivative of canarine is precipitated by adding alcohol. The precipitate is washed with alcohol and decomposed with hydrochloric acid, when canarine is obtained as a brown-red powder of somewhat metallic appearance; it is insoluble in water, alcohol, and ether, but soluble in alkalis. When dissolved in concentrated sulphuric acid, sulphurous anhydride is evolved; this distinguishes canarine from pseudosulphocyanogen. Canarine forms soluble salts with the alkali-metals, and coloured precipitates with other metals. It is the only colouring matter by which vegetable fibres can be dyed without the use of a mordant.

W. R. D.

**Dichlorether.** By K. NATTERER (*Monatsh. Chem.*, **5**, 491–507).—As the constitution of dichlorether is represented by the formula  $\text{CH}_2\text{Cl}.\text{CHCl}.\text{OEt}$ , the author anticipated being able to resolve it by heat into *monochloraldehyde* and *ethyl chloride*; the result of heating this compound in sealed tubes at 180°, is, however, to resolve it into ethyl chloride and a black pitch-like mass. This decomposition, the author considers, may be attributed to the action of a small quantity of water contained in the dichlorether, since the compound is not decomposed



when its vapours are passed through tubes heated at  $200^{\circ}$ . Dichlorether heated at  $110-120^{\circ}$  with sodium oxalate, yields a distillate containing monochloraldehyde, monochloroacetal, and hydrochloric acid, and a residue consisting of a dark liquid and sodium chloride.

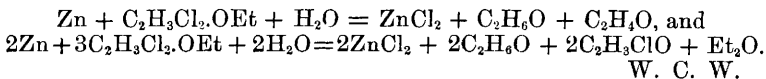
Monochloraldehyde appears to unite with alcohol, forming thick non-crystallisable liquids consisting of alcoholates, the composition of which has not been determined; a solution of monochloraldehyde in alcohol yields monochloroacetal, when allowed to remain for some time. The alcoholates and monochloroacetal are converted into dichlorether by hydrochloric acid.

Dichlorether is decomposed by alkalis; the action of baryta-water on it has been especially studied, the author expecting to obtain hydroxyaldehyde, thus:  $\text{CH}_2\text{Cl}.\text{CHCl}.\text{OEt} + \text{Ba}(\text{OH})_2 = \text{BaCl}_2 + \text{EtOH} + \text{OH}.\text{CH}_2.\text{CHO}$ . Although barium chloride and ethyl alcohol are formed, hydroxyaldehyde is not found amongst the products of this reaction, but two organic compounds are produced, whose composition has not been determined; it is possible that they owe their origin to the production of hydroxyaldehyde in some phase of the reaction.

Dichlorether is acted on by aqueous ammonia, monochloraldehyde ammonia, ethyl alcohol, and ammonium chloride being formed, thus:  $\text{CH}_2\text{Cl}.\text{CHCl}.\text{OEt} + \text{H}_2\text{O} + 2\text{NH}_3 = \text{CH}_2\text{Cl}.\text{CH}(\text{OH}).\text{NH}_2 + \text{EtOH} + \text{NH}_4\text{Cl}$ . Alcoholic ammonia, heated with monochloraldehyde-ammonia, yields an amorphous basic compound. P. P. B.

**Reactions of Dichlorether.** By J. WISLICENUS (*Annalen*, **226**, 261—281).—A complicated reaction takes place when metallic zinc is brought into contact with dichlorether, the chief products of which are zinc chloride, hydrochloric acid, ethyl chloride, ethyl alcohol, monochloraldehyde, and the condensation-product  $\text{C}_8\text{H}_{16}\text{Cl}_2\text{O}_3$ , which has been described by Abeljanz (this Journal, 1873, 154).

In the presence of water, a more simple reaction takes place, which results in the formation of ethyl ether, acetaldehyde, ethyl alcohol, and monochloraldehyde. Small quantities of crotonaldehyde, chloroacetal,  $\beta$ -hydroxydichlorether,  $\text{OH}.\text{CH}_2.\text{CHCl}.\text{OEt}$ , and the condensation-product,  $\text{CH}_2.\text{ClCH}(\text{OEt})_2\text{O}$ , are also formed. The reaction may be represented by the equations:—



**Action of Benzoic Peroxide on Amylene.** By E. LIPPMANN (*Monatsh. Chem.*, **5**, 559—566).—Benzoic peroxide and amylenes do not react at the boiling point of the latter, even in closed vessels under 2 atmos. pressure. In sealed tubes at  $100^{\circ}$  (equal to about 10 atmos. pressure), a reaction occurs of so violent a nature, that only small quantities can be operated on at a time. The products of the reaction are benzoic acid, small quantities of benzoic anhydride, pentane, and carbonic anhydride, and an oil of pleasant ethereal odour, lighter than water; it cannot be distilled without decomposition, even in a vacuum. This oil appears to be a mixture of benzoates, as on saponification with alcoholic potash it yields potas-

sium benzoate and a clear yellow oil, of which about one-half consists of an amylene oxide,  $C_{10}H_{20}O$ , boiling at  $198-203^{\circ}$  (uncorr.). It is lighter than water, has an odour resembling that of oil of rue, and does not combine with sodium hydrogen sulphite nor reduce ammoniacal silver solution. Further experiments are required to show whether it is identical with the amylene oxide obtained by Eltekoff by the action of lead oxide and water on diamylene bromide. The amylene employed in these experiments was a mixture of isomeric hydrocarbons boiling at  $35-40^{\circ}$ .  
A. J. G.

**Trichloromethylsulphonic Chloride and the Derivatives of Methylsulphonic Acid.** By G. MCGOWAN (*J. pr. Chem.* [2], 30, 280-304).—Continuing his former work on this subject (Abstr., 1884, 1126), the author has studied the reactions of methylsulphonic and dichloromethylsulphonic chlorides and their respective acids.

Methylsulphonic acid, chloride, and amide, were prepared as described by Carius (*Annalen*, 114, 142), and also the anilide; the latter crystallises in large plates, very soluble in alcohol. The chloride is not affected by sulphuretted hydrogen. All attempts to convert it into the cyanide by means of potassium cyanide failed, and the author was also unsuccessful in chlorinating methylsulphonic acid or its chloride. Trichloromethylsulphonic acid dissolves iron with evolution of hydrogen, forming the ferrous salt; tin and zinc reduce the acid. The chloride cannot be obtained from the acid or any of its salts by heating with phosphorus pentachloride. Potassium cyanide, as Loew has shown, converts the chloride in aqueous or alcoholic solution into the potassium salts of trichloromethylsulphinic and dichlorhydroxymethylsulphinic acids. From the salt of the latter acid, dichlorhydroxymethylsulphonic chloride may be obtained by treatment with phosphorus pentachloride. The corresponding anilide was also prepared and analysed.

Sulphuretted hydrogen has no action on trichloromethylsulphonic chloride when dissolved in benzene. With aniline also, the reaction proceeds according to the solvent: in alcohol and benzene, the corresponding anilide is formed, whilst in ether the products are aniline and chloraniline sulphate. Methylamine, like ammonia, evolves nitrogen when brought into contact with trichloromethylsulphonic chloride.

Dichloromethylsulphonic acid, prepared by the action of zinc on trichloromethylsulphonic acid, differs from the latter in easily yielding a chloride with phosphorus pentachloride, which is further converted into its corresponding amide by ammonia. The action of sulphuretted hydrogen and sulphurous anhydride on this chloride could not be properly studied for want of material.  
J. K. C.

**New Anhydride of Mannitol.** By SOKOLOBOFF (*Bull. Soc. Chim.*, 42, 327).—By reducing mannitol dichlorhydrin with sodium amalgam, a crystalline and a viscous substance are obtained. Both dissolve easily in water and alcohol, but are insoluble in ether. The crystalline compound melts at  $119^{\circ}$  and boils under diminished

pressure without decomposition; it has the formula  $C_6H_{10}O_4$ , and from its physical properties appears to be an isomeride of the isomannide of Fauconnier and of the mannide of Berthelot. W. R. D.

**Raffinose (Melitose ?) from Molasses.** By B. TOLLENS (*Ber.*, 18, 26—28).—The author has examined a sugar crystallising in needles obtained from a sample of molasses from cane-sugar purified by the strontium hydroxide process. This sugar after purification crystallises in white needles of the formula  $C_{12}H_{22}O_{11} + 3H_2O$ . In the hydrated condition, it melts at  $100^\circ$ , but if previously dried at  $60-80^\circ$ , it remains solid at  $130^\circ$ . A 9.5986 per cent. solution when polariscopically examined shows a specific rotation  $[\alpha]_D = 102.5-103^\circ$ . No birotation is observable. When this solution is heated with a little sulphuric acid, the specific rotation is reduced to  $45^\circ$ . The original sugar does not reduce Fehling's solution, but after treatment with acid becomes strongly reducing. When treated with nitric acid, it yields a substance melting at  $210-214^\circ$ , and more soluble than mucic acid.

This sugar appears to be identical with the raffinose obtained by Loiseau from molasses, and by Ritthausen from cotton-seed cake, and is probably identical with melitose obtained from eucalyptus-manna. Ritthausen considered his sugar to be identical with melitose (*Abstr.*, 1884, 1286), but the author points out that the rotation found by Berthelot for melitose was only about  $85^\circ$ ; it is very likely that Berthelot's melitose was impure.

This sugar has a higher rotation than cane-sugar, and is probably the cause of the high rotation of some sugars which in the trade are said to contain plus-sugar. L. T. T.

**Action of Heat on Starch Granules.** By S. SCHUBERT (*Monatsh. Chem.*, 5, 472—487).—This paper contains an account of the result of the investigation of the changes which dry starch undergoes when heated at temperatures varying from  $160-190^\circ$ ; an account is given of the change in form and structure which the granules gradually undergo under these conditions; this the author regards as due not only to a loss of water on the part of the granules, but also to the different physical and chemical behaviour of the individual layers of the granule. The microscopic examination of the granules heated at  $160^\circ$  shows the presence of gas bubbles in the centre of the starch-granule, which increase in size when the temperature is raised to  $175^\circ$ , at the same time the layers become more distinct; when the temperature is raised to  $190^\circ$ , the granule appears to be composed of a series of scales, which, by the loss of intermediate substance, seem to be separated from one another. In the conversion of starch into a soluble variety by heating it with glycerol, the author considers that the glycerol acts simply as a regulator of temperature. Starch, which by heating has been converted into a substance entirely soluble in hot water, is partially dissolved when treated with cold water, the dextrin and soluble starch produced from the granulose being dissolved, whilst the insoluble matter is represented by an organised residue, consisting chiefly of cellulose, and having

the original form of the grain: this residue is soluble in hot water, and its solutions are dextrogyrate: the specific rotation being, however, less than that of soluble starch. P. P. B.

**Action of Certain Substances on Dextrin.** By W. K. J. SCHOOR (*Chem. Centr.*, 1884, 455).—Whilst estimating glucose in a very impure commercial product containing starch, dextrin, and glucose, the amount of cuprous oxide separated was found to vary with the concentration of the liquid and the duration of heating: this was therefore effected on a water-bath below 100°. On adding a solution of salt to the mixture of dextrin and Fehling's solution, and then heating, a powerful reduction takes place, and is increased by the further addition of salt; hydrogen sodium carbonate produces the same effect. Glycerol, which alone has no reducing action on Fehling's solution, also effects a reduction when added to a solution of dextrin, and the action is even more marked when one of the above salts is employed together with glycerol. In this case, the dextrin appears to be completely converted into dextrose. The change takes place at the ordinary temperature. A. K. M.

**Optical Activity of Cellulose. Observations on a Recent Communication by M. Béchamp.** By A. LEVALLOIS (*Compt. rend.*, 99, 1122).

**Rotatory Power of Solutions of Cellulose in Schweizer's Reagent.** By A. BÉCHAMP (*Compt. rend.*, 100, 117—119).—The molecular rotatory power of cellulose, as determined by dissolving purified cotton in Schweizer's solution, is not constant but shows very wide variations. The author is of opinion that the cellulose is not simply dissolved by the reagent, but undergoes progressive molecular alterations which terminate in a constant molecular state in which the substance retains certain characteristics of cellulose, but has other properties peculiar to the particular molecular condition.

C. H. B.

**Cutose.** By E. FREMY and URBAIN (*Compt. rend.*, 100, 19—24).—The substance of this paper has already appeared elsewhere (compare Abstr., 1884, 859).

C. H. B.

**Trimethylamine and Pyrroline from Coal Gas.** By G. WILLIAMS (*Chem. News*, 51, 15—16).—In a previous communication (*Jour. Gas Lighting*, 41, 913, 960) it was shown that ammonia and another volatile base are produced when coal-gas is passed over hydrogenised palladised pumice heated much below redness. The palladised pumice is charged with hydrogen by passing coal-gas over it when heated at 100°. Finding that zinc-dust treated in a similar manner can replace the palladium, more extensive experiments have been made. A globular flask is fitted with a cork, and two tubes, one of which reaches nearly to the bottom, its lower end being protected by fine copper gauze, this tube serves for admission of gas. The flask is filled up to the neck with zinc-dust which is hydrogenised at a low temperature, and while the gas is passing, it is gradually heated

more strongly ; between 95—208°, best of all at about 117°, hydrogen sulphide, ammonia, pyrroline, and trimethylamine are recognisable among the products. The yield of these substances is extremely irregular, in one experiment 100 feet of gas yielded 1·7 grains  $\text{NMe}_3$  and 15·0  $\text{NH}_4\text{Cl}$ ; in another, 101 feet gave 0·5 grain  $\text{NMe}_3$  and 6·2  $\text{NH}_4\text{Cl}$ ; the total amount obtained in six experiments, using more than 260 feet of gas, was 7·2 grains  $\text{NMe}_3$  and 25·2  $\text{NH}_4\text{Cl}$ . In a similar manner, using hydrogen prepared from zinc and sulphuric acid instead of coal-gas, ammonia and methylamine were obtained from hydrocyanic acid. A sample of zinc-dust treated with dilute sulphuric acid, washed and dried, did not act in the manner described.

D. A. L.

**Formation of Tetramethylammonium Nitrate.** By E. DUVILLIER and H. MALBOT (*Compt. rend.*, **100**, 177—178).—When methyl nitrate (1 mol.) is mixed with concentrated aqueous ammonia (1 mol.), and the mixture allowed to remain with periodical agitation, the whole of the methyl nitrate disappears after about six weeks, and the liquid contains the different amines in the following proportions approximately:—Ammonia = 10, monomethylamine = 1½, dimethyl- and trimethyl-amines = 1, tetramethylammonium hydroxide = 6.

The volatile amines were expelled by boiling the liquid with excess of potash, and were separated by Duvillier and Buisne's method (*Ann. Chim. Phys.* [5], **22**, 319). The tetramethylammonium hydroxide was extracted from the residual liquid. When methyl nitrate and concentrated aqueous ammonia are heated in the same proportions in sealed tubes at 100°, the same products are obtained in the same proportions.

The action of methyl nitrate on aqueous ammonia differs from its action on alcoholic ammonia (Abstr., 1880, 545), in that tetramethylammonium hydroxide is formed in considerable quantity in the first case, but only in very small quantity in the second. In both cases, dimethylamine and trimethylamine are formed in very small proportions.

The action of aqueous ammonia on methyl nitrate resembles the action of ammonia gas on a solution of methyl nitrate in wood spirit (Abstr., 1884, 577).

C. H. B.

### **Action of Zinc Organo-metallic Compounds on Aldehydes.**

By E. WAGNER (*Bull. Soc. Chim.*, **42**, 330).—The reaction of zinc ethyl with saturated and unsaturated paraffinoid and benzenoid aldehydes yields secondary alcohols. Zinc methyl probably behaves in a similar way. With zinc propyl, the result is not so simple, for the propyl group is also decomposed, yielding propylene and hydrogen; the latter reduces the aldehyde to a primary alcohol. In fact, as the molecular weight of the zinc-compound becomes greater, the reaction is rendered more complicated and difficult to effect. By acting with zinc ethyl on acetaldehyde, valeraldehyde, cœnanthaldehyde, acraldehyde, and benzaldehyde respectively, the following secondary alcohols were obtained:—*Methyl ethyl carbinol*, *ethyl isobutyl carbinol*, *ethyl hexyl carbinol*, *ethyl vinyl carbinol*, and *ethyl phenyl carbinol*. The reaction of zinc propyl with cœnanthaldehyde results in the formation of a mixture of *propyl heptyl carbinol* with primary heptyl alcohol, and with acetaldehyde

in the production of *methyl propyl carbinol* and ethyl alcohol. In these reactions, the rate of chemical change depends on the relative number of carbon and hydrogen atoms in the molecule, and also on the molecular weights of the reacting bodies. It is greater with unsaturated than with saturated aldehydes, and is inversely proportional to the molecular weights of the compounds reacting. Thus with zinc ethyl and acetaldehyde, the change is instantaneous, with acetaldehyde it is complete in two or three days, with benzaldehyde in about nine days, with valeraldehyde in about a month, whilst with cænanthaldehyde the reaction is not completed until nearly two months. With zinc propyl and acetaldehyde, the completion of the change occupies from six to eight days. The method is recommended as a general one for preparing secondary alcohols.

W. R. D.

**Action of Metals on Chloral Hydrate.** By M. S. COTTON (*Bull. Soc. Chim.*, **42**, 622—625).—Zinc foil scarcely attacks an aqueous solution of chloral hydrate at the ordinary temperature, but at 80° or 100° a rapid action sets in with formation of hydrogen, methane, and zinc oxychloride. Zinc dust acts more energetically and at the ordinary temperature, the same products being formed together with chlorinated methanes, and the reaction proceeding almost on the same lines as the reduction of chloroform by zinc.

The action of iron on chloral hydrate depends on the temperature and the state of division of the metal; besides methane and chloromethanes, other products are formed the nature of which is still under investigation.

J. K. C.

**Crystallised Anhydrous Zinc Acetate.** By J. PETER and O. DE ROCHEFONTAINE (*Bull. Soc. Chim.*, **42**, 573—574).—Zinc acetate dried at 150° is boiled with pure glacial acetic acid. The filtered solution kept in a well-corked flask deposits crystals of anhydrous zinc acetate on cooling.

J. K. C.

**Compound of Ethyl Acetate with Calcium Chloride.** By J. A. LE CANU (*Compt. rend.*, **100**, 110—112).—Liebig pointed out that ethyl acetate combines with calcium chloride, but the compound formed has not previously been analysed.

When pure, dry ethyl acetate boiling at 76—77° is poured on to powdered calcium chloride, the mixture solidifies with development of heat. The product is dissolved in an excess of ethyl acetate at 40—50°, and the solution filtered and allowed to cool, when short slender needles of the composition  $2C_2H_5O_2Et, CaCl_2$  are deposited. This compound is rapidly decomposed by moist air, and when dissolved in water, the ethyl acetate is liberated. It dissolves readily in absolute alcohol. If a current of dry ammonia gas is passed into a solution of the compound in ethyl acetate, the calcium chloride is completely precipitated.

If magnesium chloride is dissolved in ethyl acetate at 70—80°, crystals resembling the calcium compound are deposited on cooling. Calcium iodide dissolves still more readily in ethyl acetate with great development of heat and formation of a very thick liquid.

C. H. B.

**Haloid Substitution Derivatives of Propionic Acid.** By L. HENRY (*Compt. rend.*, **100**, 114—117).— *$\beta$ -Chloropropionic acid*,  $\text{CH}_2\text{Cl}.\text{CH}_2.\text{COOH}$ , obtained by the decomposition of its chloride by exposure to air, forms large thin white lamellæ which are somewhat hygroscopic. It melts at  $37\text{--}38^\circ$ , and boils with slight decomposition at  $203\text{--}205^\circ$ , under a pressure of 764 mm. Unlike its isomeride, it is neither corrosive nor caustic.

*$\beta$ -Chloropropionic chloride*,  $\text{CH}_2\text{Cl}.\text{CH}_2.\text{COCl}$ , obtained by the action of phosphorus trichloride on the preceding compound, is a colourless liquid with a strong suffocating odour; it reacts violently with water, alcohol, and ammonia. It boils at  $143\text{--}145^\circ$ , under a pressure of 763 mm.; vapour-density 4.42; sp. gr. at  $13^\circ = 1.3307$ .

*Ethyl  $\beta$ -monochloropropionate*,  $\text{CH}_2\text{Cl}.\text{CH}_2.\text{COOEt}$ , prepared by the action of the acid on ethyl alcohol in presence of sulphuric acid, or better by the action of the acid chloride on alcohol, resembles the corresponding acetate, but has a less powerful odour. It boils at  $162\text{--}163^\circ$  under a pressure of 765 mm.; vapour-density 4.94; sp. gr. at  $8^\circ = 1.1160$ . Unlike the corresponding acetate, it has very little action on an alcoholic solution of sodium iodide. It differs in the same way from propyl chloracetate which resembles it in physical properties, and is obtained in a similar manner. This latter compound boils at  $161\text{--}162^\circ$  under a pressure of 765 mm.; sp. gr. at  $8^\circ = 1.1096$ .

*Methyl  $\beta$ -chloropropionate*,  $\text{CH}_2\text{Cl}.\text{CH}_2.\text{COOMe}$ , boils at  $155\text{--}157^\circ$ .

*Monochlorethyl  $\beta$ -chloropropionate*,  $\text{CH}_2\text{Cl}.\text{CH}_2.\text{COO}.\text{C}_2\text{H}_4\text{Cl}$ , obtained by the action of  $\beta$ -chloropropionic chloride on glycol-monochlorhydrin, is a colourless liquid with little odour. It is insoluble in water and boils at  $210\text{--}215^\circ$ ; sp. gr. at  $8^\circ = 1.282$ . Unlike its lower homologue, it has little action on sodium iodide in alcoholic solution.

*$\alpha$ -Monochloropropionic chloride*,  $\text{CHMeCl}.\text{COCl}$ , obtained by the action of phosphorus trichloride on  $\alpha$ -chloropropionic acid, boils at  $109\text{--}110^\circ$ , under a pressure of 744 mm.; sp. gr. at  $7.5^\circ = 1.2394$ ; vapour-density 4.38. Monochloroacetic chloride boils at  $107\text{--}108^\circ$ . The  $\alpha$ -chloropropionic derivatives closely resemble in volatility the corresponding acetic compounds.

*Methyl  $\beta$ -iodopropionate* boils without decomposition at  $188^\circ$ , under a pressure of 756 mm.; sp. gr. at  $7^\circ = 1.8408$ . *Ethyl  $\beta$ -iodopropionate* boils with slight decomposition at  $198\text{--}200^\circ$ , under a pressure of 754 mm.; sp. gr. at  $8^\circ = 1.707$ . Both compounds are colourless liquids which become brown on exposure to light. They are insoluble in water, and have an agreeable ethereal odour, which does not affect the eyes. In this respect, they differ from the corresponding acetic compounds. They are obtained by the action of  $\beta$ -iodopropionic acid on the alcohol in presence of sulphuric acid.

*Propyl iodoacetate*,  $\text{CH}_2\text{I}.\text{COOPr}$ , obtained by the action of propyl chloracetate on sodium iodide in alcoholic solution, resembles the metameric ethyl iodopropionate in its physical properties (boiling at  $198^\circ$ , under 756 mm. pressure; sp. gr. at  $7^\circ = 1.6794$ ). It differs from it by the fact that its vapour produces lachrymation.

*$\beta$ -Iodopropionamide*,  $\text{CH}_2\text{I}.\text{CH}_2.\text{CONH}_2$ , obtained by the action of aqueous ammonia on methyl  $\beta$ -iodopropionate at the ordinary temperature, forms colourless tabular crystals which become yellow when

exposed to light. They melt at 100—101°, and dissolve readily in water, yielding a solution which can be precipitated with silver nitrate.

*Iodacetamide*, obtained by the action of alcoholic ammonia on methyl iodacetate under the same conditions, forms small needles which melt at 157—158°.

C. H. B.

**$\alpha$ -Ethylamidopropionic Acid.** By E. DUVILLIER (*Compt. rend.*, **99**, 1120—1121). —  *$\alpha$ -Ethylamidopropionic acid* is obtained by the action of  $\alpha$ -bromopropionic acid on ethylamine. It crystallises from an aqueous solution in large monoclinic crystals with a rhombohedral appearance, containing  $\frac{1}{2}\text{H}_2\text{O}$ , which is gradually given off at the ordinary temperature over sulphuric acid. At 25°,  $\alpha$ -ethylamidopropionic acid dissolves in rather less than twice its weight of water, and in about 50 times its weight of alcohol. It is somewhat more soluble in boiling alcohol, from which it separates in nacreous plates on cooling. When carefully heated, the acid volatilises without melting and without decomposition. It forms a hydrochloride which crystallises in slender needles and is extremely soluble in water and in alcohol. The platinochloride is also extremely soluble in both water and alcohol, but after some time is deposited from an aqueous solution in very deliquescent slender needles. The addition of ether to the alcoholic solution precipitates the platinochloride in the form of an oil. The aurochloride forms large anhydrous golden-yellow prismatic crystals. The copper salt of  $\alpha$ -ethylamidopropionic acid is obtained by adding cupric hydroxide to an aqueous solution of the acid. It forms small deep blue anhydrous prisms, which give a pale blue powder. This salt is soluble in water and in alcohol, yielding blue solutions.

C. H. B.

**Residue obtained by the Distillation of Castor-oil in a Vacuum.** By F. KRAFFT and T. BRUNNER (*Ber.*, **17**, 2985—2987). — The formation of an elastic substance resembling caoutchouc in appearance, when castor-oil is distilled in a vacuum, has been observed by Leeds (*Abstr.*, 1883, 655), Bussy and Lecanu (*Jour. Pharm.*, **13**, 57), Stanek (*J. pr. Chem.*, **63**, 138), and Bouis (*N. Ann. Chim. Phys.*, **44**, 80). The author finds that this body is di-undecylenic acid, a polymeride of undecylenic acid, and that it is formed when undecylenic acid is heated in sealed tubes at 300°. It melts at 29—30°, boils at 275° under a pressure of 15 mm., can be crystallised from alcohol, and yields a silver salt of the composition  $\text{C}_{22}\text{H}_{38}\text{O}_4\text{Ag}$ .

W. C. W.

**Action of Ammonia on Ethyl Acetoacetate.** By J. N. COLLIE (*Annalen*, **226**, 294—322). — Ethyl acetoacetate absorbs gaseous ammonia at 0°, uniting with it to form a crystalline additive product,  $\text{OH.CMe}(\text{NH}_2).\text{CH}_2.\text{COOEt}$ , which decomposes even at 0° into water and the compound  $\text{C}_6\text{H}_{11}\text{NO}_2$ , which has been described by Precht (*Abstr.*, 1878, 970) and Duisberg (*Abstr.*, 1882, 1192). It is termed "*Ethyl paramidacetoacetate*" by the latter chemist. A better yield of the compound is obtained by passing ammonia into a mixture of absolute ether with ethyl acetoacetate, and distilling the crystalline product in a vacuum.



Ethyl paramidacetoacetate yields  $\beta$ -hydroxybutyric acid on reduction with nascent hydrogen, and a monoacetic derivative,  $\text{NHAc.CMe:CH.COOEt}$  (melting at  $63^\circ$  and boiling at  $231^\circ$ ), on treatment with acetic anhydride. As it is converted into ethyl nitrosoacetoacetate by the action of nitrous acid, it may be regarded as the ethylic salt of  $\beta$ -amido- $\alpha$ -crotonic acid.

When it is distilled under atmospheric pressure, a large quantity of a thick oily liquid is formed, from which the *ethylic salt of hydroxybutidine-monocarboxylic acid* is slowly deposited in colourless crystals melting at  $140^\circ$ :  $2\text{C}_6\text{H}_{11}\text{NO}_2 = \text{NH}_3 + \text{C}_2\text{H}_4\text{O} + \text{C}_8\text{H}_9\text{NO}_3\text{Et}$ . The free acid,  $\text{C}_8\text{H}_9\text{NO}_3 + \text{H}_2\text{O}$ , crystallises in small needles and melts at  $246^\circ$ .

The barium salt is very soluble in water, the silver salt is an unstable amorphous body, and the copper salt forms pale-blue microscopic anhydrous needles.

The *ethylic salt of dihydrocollidinedicarboxylic acid*, described by Hantzsch (Abstr., 1883, 82), is formed when a mixture of ethyl paramidacetoacetate, paraldehyde, and a small quantity of sulphuric acid is gently heated:  $2\text{C}_6\text{H}_{11}\text{NO}_2 + \text{C}_2\text{H}_4\text{O} = \text{NH}_3 + \text{H}_2\text{O} + \text{C}_{14}\text{H}_{21}\text{NO}_4$ . Ethyl paramidacetoacetate unites with two atoms of bromine, forming an unstable compound.

These results leave it undecided whether ethyl paramidacetoacetate is the ethylic salt of  $\beta$ -amido- $\alpha$ -crotonic acid,  $\text{NH}_2.\text{CMe:CH.COOEt}$ , or of  $\beta$ -imidobutyric acid,  $\text{NH:CMe.CH}_2.\text{COOEt}$ . W. C. W.

**Butyrolactone and  $\alpha$ -Ethylbutyrolactone.** By MOEHSIN BEG CHANLAROFF (*Annalen*, **226**, 325—343).—Butyrolactone is prepared by boiling the product of the action of ethylene-chlorhydrin on ethyl sodacetoacetate with baryta-water. After removing the excess of baryta with carbonic anhydride, the filtrate is evaporated to a syrup and exhausted with ether, in order to remove other products of decomposition. The residue is warmed to drive off the last traces of ether, and after the barium has been carefully precipitated as sulphate, the filtrate is repeatedly treated with ether, in order to extract the lactone. On distilling the extract, ether, water, acetic acid, and finally the lactone pass over. The lactone,  $\text{C}_4\text{H}_6\text{O}_2$ , boils at  $203^\circ$ , and remains liquid at  $-17^\circ$ . Its properties have been described by Saytzeff (*J. pr. Chem.*, **25**, 66). It is converted into a salt of  $\gamma$ -hydroxybutyric acid by boiling with an alkaline carbonate, or with baryta-water. This acid has been investigated by Saytzeff (*loc. cit.*).

Butyrolactone is very slowly converted into  $\gamma$ -hydroxybutyric acid by water at the ordinary temperature. The change takes place more rapidly with boiling water, but as a solution of  $\gamma$ -hydroxybutyric acid itself splits up into water and the lactone when boiled, a state of equilibrium is attained in 10 or 12 hours.

$\alpha$ -Ethylbutyrolactone,  $\text{C}_6\text{H}_{10}\text{O}_2$ , is formed when the ethylic salt of ethyl-hydroxyethylacetoacetate (the product of the action of ethylenechlorhydrin on ethyl sodethylacetoacetate) is decomposed by baryta-water. It is a colourless mobile liquid which boils at  $215^\circ$  and remains liquid at  $-17^\circ$ . It sp. gr. at  $16^\circ$  is 1.0348. The lactone is soluble in 10 times its volume of water at  $0^\circ$ , and is less soluble in warm water.

The cold solution becomes turbid when heated. It dissolves freely in alcohol and ether. The lactone is converted into  $\alpha$ -ethyl- $\gamma$ -hydroxybutyric acid on boiling with alkaline carbonates or with baryta-water. This acid forms a thick liquid which does not solidify at  $-17^\circ$ . The barium salt,  $\text{Ba}(\text{C}_6\text{H}_{11}\text{O}_3)_2$ , is deposited from a hot saturated alcoholic solution in crystals. The aqueous solution is decomposed by evaporation on a water-bath.

The calcium salt crystallises readily; it is freely soluble in water, sparingly soluble in absolute alcohol. The crystals contain less than 1 mol.  $\text{H}_2\text{O}$ , probably  $\frac{1}{2}$  or  $\frac{1}{3}$   $\text{H}_2\text{O}$ .

The crystalline silver salt,  $\text{C}_6\text{H}_{11}\text{O}_3\text{Ag}$ , is soluble in hot water. Ethylbutyrolactone is slowly converted into  $\alpha$ -ethyl- $\gamma$ -hydroxybutyric acid on boiling with water, and this acid readily splits up into the lactone and water, so that a state of equilibrium is soon produced.

W. C. W.

**Action of Water and of Hydriodic Acid on Valerolactone and on Isocapro lactone.** By R. FITTIG and M. RÜHLMANN (*Annalen*, **226**, 343—347).—Boiling with water converts valerolactone and isocapro lactone into hydroxyvaleric and hydroxyisocaproic acids respectively. The state of equilibrium is attained in the case of the former in four hours. The conversion of the isocapro lactone into the hydroxy-acid is less complete than that of valerolactone.

At  $200^\circ$ , hydriodic acid in presence of amorphous phosphorus acts on valerolactone, producing normal valeric acid and a neutral oil. Mielck (*Annalen*, **180**, 57) has shown that under these conditions isocapro lactone undergoes a similar change.

W. C. W.

**Condensation-products of the Lactones.** By R. FITTIG (*Ber.*, **17**, 3012—3014).—Capro- and valero-lactones unite with sodium ethylate, forming unstable compounds which are decomposed when heated at  $100^\circ$  in a flask with a reflux condenser. On the addition of hydrochloric acid to the product, oily liquids separate which exhibit the general properties of the lactones. They owe their formation to the following reactions:— $2\text{C}_6\text{H}_8\text{O}_2 - \text{H}_2\text{O} = \text{C}_{10}\text{H}_{14}\text{O}_3$  and  $2\text{C}_6\text{H}_{10}\text{O}_2 - \text{H}_2\text{O} = \text{C}_{12}\text{H}_{18}\text{O}_3$ .

These compounds dissolve slowly in warm alkalis. From the alkaline solutions, hydrochloric acid precipitates crystalline acids of the composition  $\text{C}_{10}\text{H}_{16}\text{O}_4$  and  $\text{C}_{12}\text{H}_{20}\text{O}_4$  respectively. The acids are monobasic. They are sparingly soluble in water, ether, and chloroform, and melt at  $130^\circ$  and  $160^\circ$  with decomposition, yielding carbonic anhydride and new liquid compounds lighter than water, and distilling readily with steam.

These new compounds ( $\text{C}_9\text{H}_{16}\text{O}_2$ , boiling at  $169.5^\circ$ , and  $\text{C}_{11}\text{H}_{20}\text{O}_2$ , boiling at  $209^\circ$ ) are also formed by boiling the lactones,  $\text{C}_{10}\text{H}_{18}\text{O}_3$  and  $\text{C}_{12}\text{H}_{22}\text{O}_3$ , with dilute hydrochloric acid. They are not lactones, being insoluble in alkalis, but resemble aldehydes and ketones, for they reduce ammoniacal silver solutions and unite with hydrogen sodium sulphite. They are not attacked by acetic anhydride, hydroxylamine, or nascent hydrogen, but they are easily acted on by hydrobromic acid: (1)  $\text{C}_9\text{H}_{16}\text{O}_2 + 2\text{HBr} = \text{C}_9\text{H}_{16}\text{Br}_2\text{O} + \text{H}_2\text{O}$ ; (2)  $\text{C}_{11}\text{H}_{20}\text{O}_2 + 2\text{HBr} = \text{C}_{11}\text{H}_{20}\text{Br}_2\text{O} + \text{H}_2\text{O}$ .

The first of these bromine-compounds forms beautiful crystals melting at  $42^{\circ}$ , but the second compound has not yet been obtained in the solid state.

W. C. W.

**Decomposition of  $\alpha$ -Methylpropyl- $\beta$ -hydroxybutyric Acid by Heat.** By E. J. JONES (*Annalen*, 226, 287—294).—Ethyl methylpropylacetoacetate, prepared by the action of methyl iodide on ethylic propylsodacetoacetate, is an oily liquid boiling about  $216^{\circ}$ . It is converted into the sodium salt of  $\alpha$ -methylpropyl- $\beta$ -hydroxybutyric acid by the action of sodium amalgam on its solution in alcohol and water. The free acid,  $C_8H_{16}O_3$ , is a yellow oil which does not solidify at  $-18^{\circ}$ . Its salts do not crystallise well. The zinc salt is less soluble in hot than in cold water. The acid decomposes at  $170^{\circ}$  into acetaldehyde and methylpropylacetic acid. This reaction is analogous to the decomposition of  $\alpha$ -diethyl- $\beta$ -hydroxybutyric acid by heat (*Annalen*, 201, 62).

When saponified with alcoholic potash, ethylic methylpropylacetoacetate yields methyl- $\alpha$ -secondary pentyl ketone,  $MeCO.CHMePr^{\alpha}$ , a colourless oil boiling between  $142^{\circ}$  and  $147^{\circ}$ , and methylpropylacetic acid boiling at  $193^{\circ}$ .

W. C. W.

**Decomposition of Ethyl Chlorocarbonate by Zinc Chloride.** By K. ULSCH (*Annalen*, 226, 281—286).—Ethyl chlorocarbonate is decomposed by zinc chloride, yielding ethyl chloride, carbonic anhydride, ethylene, and hydrogen chloride.

W. C. W.

**Seleniocarbamide and its Derivatives.** By A. VERNEUIL (*Compt. rend.*, 99, 1154—1157).—Ammonium seleniocyanate cannot be converted into seleniocarbamide, but is completely decomposed at  $170^{\circ}$ .

If a current of hydrogen selenide is passed into a 2 per cent. ethereal solution of cyanamide containing a small quantity of ammonia, the hydrogen selenide is almost completely absorbed, and after some hours seleniocarbamide begins to separate in crystals. In two or three days, the cyanamide is completely converted into seleniocarbamide, which can be purified by recrystallisation from water.

Seleniocarbamide,  $CSe(NH_2)_2$ , forms white odourless needles, very soluble in hot water, much less soluble in cold water, and only slightly soluble in alcohol and ether. The solutions are decomposed by light, with separation of selenium, the decomposition taking place more readily in presence of an alkali, but not in presence of free acid. Seleniocarbamide melts at about  $200^{\circ}$  and decomposes.

In presence of air at the ordinary temperature, hydracids convert seleniocarbamide into a condensed oxygenated product, oxytriseleniocarbamide,  $(CSeN_2H_4)_3O$ , which exists only in combination with acids. It has no analogue in the carbamide or thiocarbamide series. Oxytriseleniocarbamide hydrochloride,  $(CSeN_2H_4)_3O \cdot 2HCl$ , is obtained by dissolving 5 grams of seleniocarbamide in 15 times its weight of cold water slightly acidulated with hydrochloric acid, adding 10 c.c. of strong hydrochloric acid, and filtering into a large vessel, so that a considerable surface of the liquid may be exposed to the air. The solution becomes yellow and deposits the pure hydrochloride. No change

takes place in absence of air. When oxytriseleniocarbamide hydrochloride is treated with alkalis or silver oxide, a metallic chloride is formed, selenium is precipitated, and the solution contains seleniocarbamide and cyanamide. The reaction takes place in accordance with the equation:  $C_3N_6H_{12}Se_3O, 2HCl + BaO = BaCl_2 + Se + 2H_2O + 2CSe(NH_2)_2 + CN_2H_2$ . The fact that only one-third of the selenium is precipitated indicates that only one-third of this element has been oxidised.

*Oxytriseleniocarbamide hydrobromide* is obtained in the same way as the hydrochloride. Both compounds form bulky crystals which are dichroic, being brown by transmitted and violet by reflected light. They are somewhat soluble in water, but are decomposed by a large excess of this liquid with precipitation of selenium. They decompose at about  $100^\circ$  into selenium, carbonic oxide, water, ammonium cyanide, and ammonium chloride or bromide. If left in the liquid in which they are formed, the hydrochloride and hydrobromide are quickly converted into more highly oxidised products.

C. H. B.

**Aspartic Acid.** By H. SCHIFF (*Ber.*, **17**, 2929—2931).—In the preparation of aspartic acid by the action of alkalis on asparagine, the yield is very small, the chief cause being the much greater solubility of the acid in saline solutions than in pure water. The author finds that a very good yield is obtained if asparagine hydrochloride is boiled with exactly 1 molecular proportion of HCl (or 1 mol. of asparagine with 2 mols. HCl) and 1 molecular proportion of  $NH_3$  added to the product. About 10—11 per cent. solutions of hydrochloric acid and ammonia are the best to employ, so that the resulting aspartic acid crystallises from about an 11 per cent. solution of ammonium chloride. If the saline solution is more concentrated, a much larger proportion of aspartic acid remains in solution. L. T. T.

**Optically Inactive Aspartic Acid.** By A. MICHAEL and J. F. WING (*Ber.*, **17**, 2984).—By heating an aqueous solution of the hydrochloride of the ordinary active aspartic acid for some hours at  $170$ — $180^\circ$ , the authors have prepared an inactive acid identical with that obtained by Dessaignes from the ammonium salt of malic, fumaric, or maleic acid (*Compt. rend.*, **30**, 324; **31**, 432), and further investigated by Wolf (*Annalen*, **75**, 293) and Pasteur (*Ann. Chim. Phys.* [3], **34**, 30).

L. T. T.

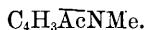
**Two Tin Organic Compounds.** By O. W. FISCHER (*Monatsh. Chem.*, **5**, 426—431).—By careful addition of *stannic chloride* to absolute alcohol, a compound identical with that described by Kuhlmann (*Annalen*, **33**, 97 and 192) is obtained; it may be crystallised from ether or alcohol, and is decomposed by heat. The analysis of this compound shows it to have the composition  $SnCl_3.OEt + EtOH$ : it is decomposed by water, forming *tin oxychloride*. By acting on *stannic chloride* with an alcoholic solution of *sodium ethylate* and evaporating the alcoholic solution, the compound  $Sn(OH)_3Et$  is obtained as an amorphous mass; it is decomposed by water with formation of stannic acid.

P. P. B.

**Action of Organic Anhydrides on Pyrroline.** By G. CIAMICIAN and M. DENNSTEDT (*Ber.*, 17, 2944—2961).—Many of the results described in this paper have already been given (*Abstr.*, 1884, 289 and 1044). The authors propose the adoption of the following radicals in the nomenclature of the pyrroline derivatives:  $\{C_4H_3(NH).CO\}'$  *pyrroyl*,  $\{C_4H_3(NH)\}'$  *pyrryl*,  $\{C_4H_2(NH)\}''$  *pyrrylene*, and  $\{C_4H_3N\}''$  *pyrrylene*.

The vapour-density of pseudacetopyrroline was taken by V. Meyer's method, and agreed with the formula  $(C_4H_3NH).COMe$ . With phenylhydrazine, pseudacetopyrroline yields white needles which melt at  $146-147^\circ$ , and have the formula  $(C_4H_3NH).CMe:N_2HPh$ . This compound is soluble in benzene, sparingly so in boiling water, and turns of a dirty-green colour on keeping. Hydrochloric acid decomposes it into its constituents. With benzaldehyde, pseudacetopyrroline yields *pseudocinnamylpyrroline*,  $C_4H_4N.CO.CH:CHPh$ . This crystallises in yellow needles, melts at  $141-142^\circ$ , and is sparingly soluble in alcohol, insoluble in water. It yields a *silver compound*,  $C_4H_3NAg.CO.CH:CHPh$ , insoluble in water. Bromine forms substitution, but no additive products. The monobromo-compound melts at about  $175-177^\circ$ , the dibromo-derivative at about  $225^\circ$ ; but these substances were not obtained in a pure state. The authors attempted to obtain a pyrrolinecarboxylic acid by the oxidation of pyrrolineglyoxylic acid,  $C_4H_4N.CO.COOH$  (acetylpyrrolinecarboxylic acid, *Abstr.*, 1884, 290), but without success, the acid being completely decomposed. *Methyl pyrrolineglyoxylate*, obtained by the action of methyl iodide on the silver salt, crystallises in colourless plates which melt at  $70-72^\circ$ , and boil with partial decomposition at  $285^\circ$ . It is easily soluble in ether, benzene, and boiling alcohol, sparingly so in water. The crystals belong to the monoclinic system, and gave  $\eta = +X:Z = 92^\circ 15' 10''$  and  $a:b:c = 1.16058:1:1.47454$ .

*Methylpyrroline* was obtained by Bell from methylammonium mucate (*Abstr.*, 1879, 525). The authors have obtained it by the action of methyl iodide on the sodium compound of pyrroline. There is scarcely any action between these substances under the ordinary pressure; but if the mixture be simply enclosed in a sealed tube, an energetic action very soon takes place; the reaction should, however, be completed by heating. Methylpyrroline is a colourless oil boiling at  $114-115^\circ$  (col. in vap.) at  $747.5$  mm. It has an odour resembling, but quite distinct from that of pyrroline. When heated with acetic anhydride, methylpyrroline yields *pseudacetomethylpyrroline*,



This substance is a colourless oil, which is heavier than water and boils at  $200-202^\circ$ . It is sparingly soluble in water, and does not form a silver derivative. It is thus clear that the replacement of the imidic hydrogen in pyrroline derivatives by alkyl radicals does not prevent the formation of acetyl derivatives. All attempts to prepare this substance by the action of methyl iodide on the silver derivative of pseudacetopyrroline proved futile, pseudacetopyrroline being regenerated. *Dipseudaceto-pyrroline* (*pyrrylene dimethyl ketone*),  $C_4H_2NHAc_2$ , is obtained when pseudacetopyrroline is heated with

excess of acetic anhydride in closed tubes at 230—250°. It crystallises in colourless needles which melt at 161—162°. It dissolves in boiling potash, and, on cooling, the potassium derivative is precipitated in white needles; the silver derivative is a white powder. It combines with benzaldehyde and forms *dipseudocinnamylpyrroline*,  $C_4H_2NH:(CO.CH:CHPh)_2$ . This body crystallises in small needles or plates, and melts at 238—240°. It is sparingly soluble in boiling alcohol, more freely so in glacial acetic acid. It dissolves in concentrated sulphuric acid with intensely violet coloration, and on this solution being added to water, a white flocculent precipitate is formed.

When a mixture of pyrroline, benzoic anhydride, and sodium benzoate is heated for about 8 hours at 200—240°, *pseudobenzopyrroline* (*pyrryline phenyl ketone*),  $C_4H_3NH_2.COPh$ , is formed, but the yield is small, a large quantity of the pyrroline becoming resinified. This substance forms white needles or scales which melt at 77°. It is easily soluble in alcohol, sparingly in boiling water; it yields a very unstable silver derivative. Together with this compound, there appears to be a small quantity of a more volatile oil formed. This is probably benzopyrroline, but the authors have not isolated it.

If 5 grams pyrroline are heated in closed tubes at 180—190° with about 3 times its volume of glacial acetic acid and 11 grams phthalic anhydride, a substance is obtained which has the formula  $C_{12}H_7NO_2$ ; it crystallises in silky yellow needles, and melts at 240—241°. It is soluble in ether, sparingly so in alcohol, and insoluble in water. No silver derivative could be obtained. It has the properties of an anhydride, and when boiled with dilute aqueous potash, dissolves to a yellow solution, which, on cooling, deposits the potassium salt in white scales. This salt yields an acid,  $C_{12}H_9NO_3$ , which is soluble in alcohol and ether, sparingly so in water, and crystallises in needles melting at 240—241°. It is easily converted into the anhydride by heating or even by repeated evaporation on the water-bath. The acid yields a silver salt,  $C_{12}H_9NO_3Ag$ . The *methyl salt*,  $C_{12}H_8NMeO_3$ , can be obtained from the silver salt or from the acid by means of alcohol and hydrochloric acid. It crystallises in prisms melting at 104—105°, and is soluble in alcohol and benzene, sparingly so in water. Like the acid, the ether is very readily converted into the anhydride when heated. Measurements of the crystals showed that they belong to the monoclinic system, and gave the following numbers:— $\eta = +X : Z = 107^\circ 14' 2''$  and  $a : b : c = 1.40305 : 1 : 1.01756$ .

The anhydride has probably one of the two following formulæ:— $CO<\overset{\cdot}{C_6H_4}>CO$  or  $CO<\overset{\cdot}{C_6H_4}>C(C_4H_3N)$ .

No hydroxylamine compound could be obtained, and the authors therefore believe the second formula to be the correct one, and the substance to be *pyrrolinephthalide*.  
L. T. T.

**Formation of Parabromobenzyl Bromide by the Action of Bromine on Parabromotoluene at the Ordinary Temperature.** By J. SCHRAMM (*Ber.*, 17, 2922—2925).—The investigations of Beilstein, Kuhlberg, Jackson, and others have shown that the

displacement of hydrogen in the side-chain of toluene and its homologues by bromine can only be effected at or near the boiling point of the hydrocarbon. The author finds that with parabromotoluene no such high temperature is necessary. The reaction was carried out at  $0^\circ$  with a solution of parabromotoluene in chloroform; with melted parabromotoluene at  $29^\circ$ ; and with crude bromotoluene (a mixture of ortho and para) at the ordinary temperature. No iodine must be added, and the reaction is much more rapid in direct sunlight than in diffused daylight. In each case, parabromobenzyl bromide, melting at  $61-62^\circ$ , was obtained, identical with that described by Jackson and Field (Abstr., 1880, 878). The yield with pure parabromotoluene is almost the theoretical. The product of the reaction of toluene at  $0^\circ$  with insufficient bromine for the formation of a mono-substitution-derivative, was found to contain the bromide.

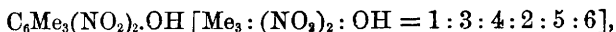
The author believes this peculiar reaction to be due to the repellant influence of the two bromine-atoms on one another already noticed by V. Meyer and others. He also points out that parabromobenzyl chloride was obtained by Jannasch as early as 1874 (this Journal, 1875, 888).

L. T. T.

**Pseudocumenol.** By K. AUWERS (*Ber.*, 17, 2976—2983).—The author has obtained a number of derivatives of pseudocumenol,  $C_6H_2Me_3.OH$  [Me : Me : Me : OH = 1 : 3 : 4 : 6].

*Trimethylorthohydroxybenzaldehyde*,  $OH.C_6HMe_3.CO.H$  [1 : 3 : 4 : 6 : 5], was obtained by acting on pseudocumenol, in alkaline solution, with chloroform. The solution must be kept dilute or the cumenol resinifies. The aldehyde crystallises in pale yellow needles, which are insoluble in cold water, soluble in alcohol, ether, chloroform, and glacial acetic acid, and melt at  $105-106^\circ$ . It sublimes undecomposed, and yields a mirror with an ammoniacal solution of a silver salt. It has the general properties of an orthoaldehyde; volatilises in a current of steam, gives a blue coloration with ferric chloride, and an intense yellow with ammonia. The yield of this compound is, however, small, owing to the formation in much larger quantity of a compound,  $C_{10}H_{12}Cl_2O$ ; the latter crystallises in prisms and plates, insoluble in water and alkalis, soluble in alcohol, ether, &c. It may be heated with alkalis or even concentrated sulphuric acid at  $100-110^\circ$  without decomposition, but resinifies at a higher temperature. The author is inclined to look upon it as a dichloromethyl ether of pseudocumyl,  $C_6H_2Me_3.O.CHCl_2$ .

*Metanitropseudocumyl nitrate*,  $NO_2.C_6HMe_3O.NO_2$  [Me : NO<sub>2</sub> : NO<sub>2</sub> = 1 : 3 : 4 : 2 : 6], is obtained by gradually adding pseudocumenol to six times its weight of well-cooled fuming nitric acid. It crystallises in rhombic prisms and tables, and melts with decomposition at  $84^\circ$ . It is very unstable, being decomposed by water at  $40^\circ$ , and by alcohol and ether at even lower temperatures into nitrous acid and a resinous body which still contains nitrogen, and is probably nitropseudocumenol. When reduced with tin and hydrochloric acid, the nitrate yields *metamidopseudocumenol*, which is soluble both in acids and alkalis, and is identical with the hydroxycumidine described by Liebermann and v. Kostanecki (Abstr., 1884, 1146).

*Dinitropseudocumenol,*

was obtained from the nitrate described above by a peculiar reaction with ammonia. Aqueous ammonia decomposes the nitrate in the same way as the fixed alkalis, water, &c., do, but alcoholic ammonia yields a red substance (probably an unstable ammonia compound), which, on neutralisation of the ammonia, yields the dinitro-compound. This substance forms groups of yellow crystals which melt at  $110^\circ$  without decomposition. It is insoluble in cold water, soluble in alcohol, ether, &c. It is decomposed by boiling with water or alcohol, and explodes when heated above its melting point.

The pseudocumenol employed in this investigation was prepared from pseudocumidine sulphate by means of the diazo-reaction. From the resin, which is always formed in considerable quantity, the author succeeded in isolating *dipseudocumenol* or *hexamethyldiphenol*,  $\text{HO.C}_6\text{HMe}_3.\text{C}_6\text{HMe}_3.\text{OH}$ . This compound melts at  $172^\circ$  and crystallises in white needles which are soluble in glacial acetic acid and in alkalis. It is identical with the compound obtained by Hofmann by the decomposition of diazo-cumidine with alcohol (Abstr., 1884, 1315). The same compound was obtained by the oxidation of pseudocumenol in acetic solution with potassium dichromate. The *methyl ether* was obtained by the action of caustic potash and methyl iodide on the dicumenol. It crystallises in white needles melting at  $124^\circ$ .

L. T. T.

**Mixed Ethers of Resorcinol.** By G. SPITZ (*Monatsh. Chem.*, **5**, 488—490).—The following ethers have been prepared by heating monomethyl resorcinol with potassium alkyl sulphates and caustic potash in sealed tubes at  $170^\circ$ . They are all colourless liquids of agreeable odour, and miscible with alcohol, ether, glacial acetic acid, benzene, &c., but insoluble in water; they are volatile in steam, and can be distilled without decomposition:—*Methyl ethyl resorcinol*,  $\text{OMe.C}_6\text{H}_4.\text{OEt}$ , boils at  $216^\circ$ ; *methyl propyl resorcinol*,  $\text{OMe.C}_6\text{H}_4.\text{OPr}$ , boils at  $226^\circ$ ; *methyl isobutyl resorcinol*,  $\text{OMe.C}_6\text{H}_4.\text{OC}_4\text{H}_9$ , boils at  $234^\circ$ ; *methyl isoamyl resorcinol* appears to boil at  $236^\circ$ . P. P. B.

**Colouring Matter from Paramidophenol.** By NOELTING and WEINGARTNER (*Bull. Soc. Chim.*, **42**, 339).—The authors are investigating the violet colouring matter which is formed when hydrogen sulphide and ferric chloride react with paramidophenol.

W. R. D.

**Ethylparatolynitrosamine.** By GASTIGER (*Bull. Soc. Chim.*, **42**, 338).—This compound has the constitution represented by the formula  $\text{C}_6\text{H}_4\text{Me.NEtNO}$  [ $\text{Me} : \text{NEtNO} = 1 : 4$ ]. From it, the author prepared pure ethylparatoluidine and studied the diazoamido-derivatives of this base.

W. R. D.

**Xylidines.** By NOELTING and FOREL (*Bull. Soc. Chim.*, **42**, 332—334, and 338—339).—Pure ortho-xylene when dissolved in sulphuric acid and nitrated with the theoretical quantity of nitric acid, furnishes



two isomeric nitro-derivatives. One is crystalline, the other liquid. The former has previously been obtained by the action of fuming nitric acid on ortho-xylene, and on reduction yields crystalline ortho-xylidine; it melts at  $29^\circ$ , and boils at  $256^\circ$ . The liquid nitro-xylene boils at  $250^\circ$ , and when reduced by iron and acetic acid it yields a new liquid ortho-xylidine, mixed with a small quantity of solid ortho-xylidine. The new compound, which is the sixth isomeride predicted by theory, is obtained pure by treating the mixture with acetic anhydride, and purifying the aceto-xylidine melting at  $134^\circ$  by fractional crystallisation. This, when saponified, yields the new ortho-xylidine,  $C_6H_3Me_2.NH_2$  [Me : Me :  $NH_2$  = 1 : 2 : 3], in the form of a liquid boiling at  $223^\circ$ , and having at  $15^\circ$  a sp. gr. of 0.991. It yields ortho-xylenol when the diazo-derivative is boiled with water, and when oxidised with the chromic mixture is converted into *ortho-xyloquinone*, crystallising in fine yellow needles and melting at  $55^\circ$ . A mixture of this xylidine with paratoluidine does not yield rosaniline when oxidised with arsenic acid. The corresponding quinol melts with decomposition at  $221^\circ$ . The authors have prepared symmetrical metaxylidine,  $C_6H_3Me_2.NH_2$  [Me : Me :  $NH_2$  = 1 : 3 : 5], by Wroblewski's method, and by oxidising it have obtained *metaxyloquinone*. This forms yellow needles which melt at  $73^\circ$ ; the corresponding quinol crystallises in white needles, and melts at  $145^\circ$ . Symmetrical metaxylenol melts at  $68^\circ$ , and resembles in properties its solid isomerides. There are now six known xylenols, five of which are solid and one [1 : 3 : 4] liquid.

Paraxyloquinone was prepared from paraxylidine; it melts at  $123^\circ$ , and is identical with the quinone already described by Nietzki and Carstanjen.

Starting with the five known xylidines, two ortho-, one para-, and two meta-, the two last melting at  $134^\circ$  and  $135^\circ$  respectively, the amido-azo-derivatives were prepared, and their constitution determined. They may be summarised as follows:—

$C_6H_3MeMe.N$	$N.C_6H_2MeMe.NH_2$	melts at $110.5^\circ$ .
$C_6H_3MeMe.N$	$N.C_6H_2MeMe.NH_2$	,, 179
$C_6H_3MeMe.N$	$N.C_6H_2MeMe.NH_2$	,, 78
$C_6H_3MeMe.N$	$N.C_6H_2MeMe.NH_2$	,, 95
$C_6H_3MeMe.N$	$N.C_6H_2MeMe.NH_2$	,, 150
$C_6H_3MeMe.N$	$N.C_6H_2MeMe.NH_2$	,, 110—111°

The last of these compounds was obtained from a mixture of unsymmetrical xylidine with paraxylidine. It has been previously obtained by Nietzki from commercial xylidine.

The authors find that when metaxylene is nitrated with sulphuric and nitric acids, in addition to ordinary nitro-xylene, the 1 : 3 : 2 isomeride is also produced. The two compounds may be separated by

fractional distillation, the new nitro-xylene passing over at 222—227°; its boiling point when pure is 225° (compare Grevingk, this vol., p. 144). By reducing the fractions obtained between these temperatures, a xylidine is formed which is identical with that obtained by Schmitz from amidomesitylenic acid. After purification by conversion into the acetyl derivative (m. p. 175°), it boiled at 214·5°. The constitution of the compound is represented by the formula

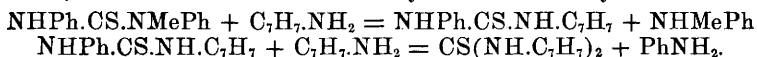


W. R. D.

**New Cumidine.** By NÖLTING and KOHN (*Bull. Soc. Chim.*, **42**, 340).—A new cumidine was prepared by heating the hydrochloride of symmetrical metaxyldine with methyl alcohol. This isocumidine, which is in all probability derived from the 1 : 2 : 3 trimethylbenzene, melts at 69°, and distils about 245°.

W. R. D.

**Secondary Amines. II.** By W. GEBHARDT (*Ber.*, **17**, 3033—3043). A continuation of the author's work on this subject (*Abstr.*, 1884, 1320). Methylthiophenylthiocarbamide is converted into methylaniline and monophenylthiocarbamide, melting at 153°, by the action of alcoholic ammonia at 100°, and into diorthotolylthiocarbamide and aniline by the action of orthotoluidine. The latter doubtless takes place in two stages: phenyltolylthiocarbamide is formed in the first instance, and is then converted into ditolylthiocarbamide by the toluidine,



Ethylthiophenylthiocarbamide, when boiled with aniline, is decomposed into ethylaniline and thiocarbanilide. Phenylmethylorthotolylthiocarbamide, melting at 121°, splits up on boiling with aniline into diphenylthiocarbamide, orthotoluidine, and methylaniline, but the corresponding para-compound under similar treatment yields phenylparatolylthiocarbamide and methylaniline.

*Allylphenylethylthiocarbamide*,  $\text{C}_3\text{H}_5\text{.HN.CS.NEtPh}$ , is formed by mixing together ethylaniline and allylthiocarbamide. It is a crystalline substance melting at 26° and dissolving freely in the usual solvents.

*Symmetrical dimethylphenylthiocarbamide*,  $\text{MeHN.CS.NMePh}$ , crystallises in transparent prisms melting at 114°, and is soluble in alcohol.

*Methylphenylethylthiocarbamide*,  $\text{MeHN.CS.NEtPh}$ , and the preceding compound are decomposed by boiling with aniline, yielding diphenylthiocarbamide.

*Methylphenylthiocarbamide*, prepared from methylcarbimide and aniline, crystallises in six-sided plates which melt at 113° and dissolve freely in alcohol.

*Diethylallylthiocarbamide*,  $\text{C}_3\text{H}_5\text{HN.CS.NEt}_2$ , is deposited from its solution in alcohol or benzene, in long needle-shaped prisms melting at 55°.

*Diethylorthotolylthiocarbamide*,  $\text{C}_7\text{H}_7\text{HN.CS.NEt}_2$ , melting at 102°, is decomposed, by boiling with aniline, into diethylamine and orthotoluidine.

Diethylamine combines with phenyl isocyanate, forming *diethylphenylcarbamide*,  $\text{PhHN.CO.NEt}_2$ , a crystalline compound melting at 85°, soluble in alcohol and benzene.

*Di-β-naphthylphenylcarbamide*,  $\text{PhHN.CO.N}(\text{C}_{10}\text{H}_7)_2$ , prepared by the action of carbanil on di-β-naphthylamine, forms soft, white needle-shaped crystals melting at  $179^\circ$ , soluble in hot alcohol.

Piperidine combines with phenylthiocarbamide, forming *piperidylphenylthiocarbamide*,  $\text{PhHN.CS.N}:\text{C}_6\text{H}_{10}$ , which crystallises in thick needles melting at  $98^\circ$ .

*Piperidylorthotolylthiocarbamide*, and the corresponding *para*-compound, are deposited from their alcoholic solutions in prisms which melt respectively at  $98^\circ$  and  $132^\circ$ . *Piperidylmethylthiocarbamide*,  $\text{MeHN.CS.N}:\text{C}_6\text{H}_{10}$ , crystallises in rhombic prisms soluble in alcohol, and melts at  $125^\circ$ . *Piperidylphenylcarbamide*,  $\text{PhHN.CO.N}:\text{C}_6\text{H}_{10}$ , formed by the action of carbanil on piperidine, crystallises in prisms, melts at  $168^\circ$ , and dissolves in alcohol and benzene. *Piperidylthiocarbamide*,  $\text{H}_2\text{N.CS.N}:\text{C}_6\text{H}_{10}$ , is prepared by evaporating a solution of piperidine sulphate and potassium thiocyanate to dryness, and extracting the residue with alcohol. It crystallises in four- or six-sided plates, and melts at  $92^\circ$ . The crystals are soluble in alcohol, water, warm acetone, and warm chloroform.

*Conylphenylthiocarbamide*,  $\text{PhHN}:\text{CS.N}:\text{C}_8\text{H}_{16}$ , forms silky needles or prisms, soluble in alcohol, and melts at  $88^\circ$ . *Conylphenylcarbamide*,  $\text{PhHN.CO.N}:\text{C}_8\text{H}_{16}$ , dissolves freely in all the ordinary solvents, and is with difficulty obtained in a pure state.

*Methylphenylurethane*,  $\text{NMePh.CO.OEt}$ , is prepared by slowly adding ethyl chlorocarbonate to methylaniline largely diluted with ether. Methylaniline hydrochloride is deposited, and the urethane remains in solution:  $2\text{NHMePh} + \text{COCl.OEt} = \text{NMePh.CO.OEt} + \text{NHMePh.HCl}$ . The urethane is an oily liquid boiling at  $244^\circ$ . W. C. W.

**Ethenyldiphenyldiamine.** By NÖLTING and WEINGARTNER (*Bull. Soc. Chim.*, **42**, 334).—Acetanilide hydrochloride when heated at  $250^\circ$  in a sealed tube for one hour, yields *ethenyldiphenylamidine hydrochloride*,  $\text{NHPh.CMe}:\text{NPh.HCl}$ , but if heated at  $300\text{--}330^\circ$  for 12–15 hours, bases of the quinoline series are obtained, together with aniline and tarry compounds. Two of the quinoline bases were isolated, one of the formula  $\text{C}_{11}\text{H}_{11}\text{N}$ , boiling at  $265\text{--}268^\circ$ , the other of the formula  $\text{C}_{12}\text{H}_{13}\text{N}$ , boiling at  $283\text{--}285^\circ$ . Tarry compounds are formed when these compounds are heated with phthalic anhydride.

W. R. D.

**Derivatives of Cumidine and Amidoazobenzene.** By NÖLTING and BAUMANN (*Bull. Soc. Chim.*, **42**, 335).—Amidoazocumene melting at  $138^\circ$  yields, on reduction, an orthodiamine of the constitution

$$\overset{1}{\text{C}_6\text{H}_2}\overset{2}{\text{Me}}\overset{4}{\text{Me}}\overset{5}{\text{Me}}.\text{N}:\text{N}.\overset{1}{\text{C}_6\text{H}_2}\overset{2}{\text{Me}}\overset{4}{\text{Me}}\overset{5}{\text{Me}}.\text{NH}_2.$$

Pseudocumenol,  $\text{C}_6\text{H}_2\text{Me}_3.\text{OH}$ , from pseudocumidine, readily combines with diazo-derivatives. Pseudocumidine hydrochloride, when heated with methyl alcohol at  $300^\circ$  in a sealed tube, yields *tetramethylamidobenzene*,  $\text{C}_6\text{HMe}_4.\text{NH}_2$ , which boils near  $250^\circ$ , and forms an acetyl-derivative melting at  $210^\circ$ . The same base is obtained when mesidine hydrochloride is treated in a similar manner. The new amine therefore has the constitution



By nitrating a solution of amidoazobenzene in sulphuric acid, an isomeride of the nitroamidoazobenzene, prepared by Nölting and Binder, is obtained. Its constitution has not yet been established. By methylating paradimethylamidoazobenzene,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4\text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , the *tetramethylazyline* of Lippmann and Fleissner is obtained.

W. R. D.

**Azo-derivatives.** By NÖLTING and BAUMANN (*Bull. Soc. Chim.*, 42, 340).—By heating dimethylamidoazobenzene with sulphuric acid at  $100^\circ$  *dimethylamidoazobenzenesulphonic acid* is obtained; on reduction, it yields sulphanilic acid, together with *dimethylparaphenylenediamine*. The sulphonic acid, therefore, has the constitution



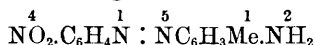
and is identical with the acid which is produced by the reaction of *paradiazophenylsulphonic acid* with *dimethylaniline*. The sulphonic acid of *paratolylazodimethylaniline* has an analogous structure, for on reduction it yields *dimethylphenylenediamine* and *amidocresylsulphonic acid*.

W. R. D.

**Diazoamido-derivatives.** By NÖLTING and BINDER (*Bull. Soc. Chim.*, 42, 336—337, and 341—342).—By the reaction of *paradiazotoluene chloride* with *aniline*, and of *diazobenzene chloride* with *paratoluidine*, a diazo-amido-compound is obtained, which, when dissolved in benzene and treated with bromine, forms *diazotoluene bromide* and *tribrom-aniline*. Hence the derivative has the constitution  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2 \cdot \text{NHPh}$ . When boiled with dilute acids, it yields *toluidine* and *phenol*, together with *cresol* and *aniline*, and, when reduced by stannous chloride, *phenylhydrazine* and *paratoluidine* are formed. The diazo-amido-derivative formed when *parabromo-diazobenzene chloride* reacts with *aniline*, or *parabromaniline* with *diazobenzene chloride*, yields *brom-aniline* and *phenol* when boiled with dilute acids. Both the foregoing compounds have been described by Griess. With *aniline*, *paranitro-diazobenzene chloride* forms a derivative which, under the influence of dilute acids, yields *nitraniline* and *phenol*; when it is heated with *aniline*, *amidoazobenzene*, *nitraniline* and a small quantity of *paranitramidoazobenzene* are produced. The latter compound melts at  $203$ — $205^\circ$ , and on reduction yields symmetrical *diamidoazobenzene*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , the parent base of the azylines.

*Methylaniline* and *diazobenzene chloride* furnish a derivative, which, on reduction, forms *phenylhydrazine* and *methylaniline*.

*Diazobenzene chloride* does not react with *paranitraniline*. *Nitro-diazobenzene chloride* does not react with *methylaniline* to form a *diazamido-derivative*, but yields an isomeric *amidoazo-compound* of the formula  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NHMe}$ . When *nitrodiazobenzene chloride* is acted on by *toluidine*, a *diamidoazo-compound* is obtained, which reacts with *orthotoluidine*, forming *amidoazotoluene*, together with a *nitro-derivative*, melting at  $198^\circ$ , of the formula



This yields *methylazyline* when carefully reduced.

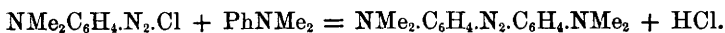
The *diamidoazo-derivative* obtained by acting on *nitrodiazobenzene*

chloride with paranitrotoluidine reacts with aniline, forming chiefly nitroamidoazobenzene.

The product of the action of ethylaniline on diazobenzene chloride is a substance of formula  $\text{PhN} : \text{N} \cdot \text{NPhEt}$ , whilst with diazotoluene chloride it yields  $\text{C}_6\text{H}_4\text{MeN} : \text{N} \cdot \text{NPhEt}$ . These compounds are decomposed when boiled with dilute acids; the first yields phenol and ethylaniline, the second paracresol and ethylaniline. An isomeric derivative of the toluene derivative has been prepared by Gastiger, by acting on diazobenzene chloride with methyl paratoluidine. It has the formula  $\text{PhN} : \text{N} \cdot \text{N} \cdot \text{EtC}_6\text{H}_7$ , and forms crystals which melt at  $38-39^\circ$ . It yields phenyl- and ethyl-paratoluidine when heated with dilute acid, whilst on reduction it forms paratoluidine and phenylhydrazine. The methyl derivative of this compound forms crystals which melt at a low temperature. Two nitro-derivatives have been obtained, melting respectively at  $55^\circ$  and  $104-105^\circ$ . When boiled with dilute acids, all these derivatives yield ethylparatoluidine, together with paracresol in the case of the methyl derivative, metanitrophenol in that of the first nitro-derivative, and paranitrophenol in that of the second.

W. R. D.

**Tetramethylazyline.** By NÖLTING and KOHN (*Bull. Soc. Chim.*, **42**, 334).—By acting with dimethylaniline on the diazo-derivative of dimethylparaphenylenediamine, symmetrical *tetramethyldiamidoazobenzene* is obtained,



This compound is identical with the tetramethylazyline described by Lippmann and Fleissner.

W. R. D.

**New Synthesis of Pararosaniline.** By J. ZIMMERMANN and A. MÜLLER (*Ber.*, **17**, 2936—2938).—If a mixture of 20 grams paranitrobenzylidene bromide and 25 grams aniline is gradually heated, the anilide is formed. If the heating be continued to  $145^\circ$ , an energetic reaction takes place, the temperature of the mixture rises quickly to  $200^\circ$ , and the whole has the appearance of a magenta-melt. From this melt, the authors have succeeded in isolating pararosaniline. The residue insoluble in water dissolves readily in alcohol, and is a colouring matter of slightly bluer shade than pararosaniline. The authors believe it to be a phenylated pararosaniline formed by the further action of the excess of aniline. The authors endeavoured to prepare paranitrobenzylidene chloride in order to investigate the action of aniline on this compound, but up to the present without success.

L. T. T.

**A New Resorcinol Blue.** By R. BENEDICT and P. JULIUS (*Monatsh. Chem.*, **5**, 534—535).—By heating together 55 grams of resorcinol with 18 grams of sodium nitrite at  $130^\circ$ , a blue colouring matter is obtained which dissolves in water, forming a dirty bluish-violet solution, and is soluble in alcohol and in sulphuric acid forming blue solutions. This colouring matter is reduced by zinc-dust in presence of an alkali, forming colourless solutions which are oxidised

easily by exposure to the air, with reproduction of the blue compound. P. P. B.

**Action of Acetamide on Phenylcyanamide.** By F. BERGER (*Monatsh. Chem.*, 5, 451—471).—With the expectation of obtaining a phenylacetoxylguanidine, the author heated together a mixture of 2 parts by weight of phenylcyanamide and 1 of acetamide. The reaction which takes place is of a complex character, ammoniacal vapours, and also those having an odour of nitrile compounds being produced, whilst a sublimate of ammonium carbonate is formed, and a residue is left from which water dissolves out acetanilide. The residue, after extraction with water, yields to boiling alcohol, a mixture of two bases which can be separated by the different solubilities of their hydrochlorides in alcohol. The less soluble hydrochloride crystallises from alcohol in silky needles of the composition  $C_{39}H_{35}N_{11}, 2HCl + 3\frac{1}{2}EtOH$ ; by decomposition with caustic potash it yields the base  $C_{39}H_{33}N_{11}$ ; this crystallises in needles melting at  $222^{\circ}$ . The solution of the base in glacial acetic acid yields with bromine a compound,  $C_{39}H_{29}N_{11}Br_6$ , crystallising from glacial acetic acid in small grains composed of microscopic needles. Nitric acid converts the base into a yellow compound which is turned to a dark red colour by alkalis. The base heated in sealed tubes with hydrochloric acid at  $150^{\circ}$  yields aniline, at  $200$ — $250^{\circ}$ , aniline and ammonia.

The soluble hydrochloride yields a base,  $C_{15}H_{16}N_6$ , melting at  $212$ — $213^{\circ}$ ; it is easily soluble in alcohol, ether, and glacial acetic acid, and sparingly soluble in hot benzene. Its hydrochloride,  $C_{15}H_{16}N_6.HCl$ , crystallises from alcohol in shining needles melting at  $252^{\circ}$ . Besides these substances, the product of the reaction of phenylcyanamide and acetamide contains a substance insoluble in the ordinary solvents, the composition of which has not been ascertained. P. P. B.

**Action of Ammonia and Amines on Thiocarbamides.** By W. GEBHARDT (*Ber.*, 17, 3043—3046).—Alcoholic ammonia at  $100^{\circ}$  converts thiocarbanilide into monophenylthiocarbamide and aniline, and it decomposes di- $\beta$ -naphthylthiocarbamide into  $\beta$ -naphthylamine and mononaphthylthiocarbamide melting at  $180^{\circ}$ .

Amines replace the two tolyl-groups in di-orthotolylthiocarbamide; thus with aniline the following reaction takes place:  $CS(NHC_7H_7)_2 + 2PhNH_2 = CS(NHPh)_2 + 2C_7H_7.NH_2$ .

Di-paratolylthiocarbamide does not appear to undergo an analogous decomposition. Aniline converts metamnonitrophenylthiocarbamide into metanitrilaniline and thiocarbanilide. It also decomposes toluylenedithiocarbamide,  $C_7H_6:(NH.CS.NH_2)_2$ , and toluylenediphenyldithiocarbamide,  $C_7H_6:(NH.CS.NHPh)_2$ , forming toluylenediamine and thiocarbanilide. W. C. W.

**A Reaction of Aldehydes.** By A. CALM (*Ber.*, 17, 2938—2941).—Amidodimethylaniline,  $NH_2.C_6H_4.NMe_2$ , reacts very readily with aldehydes both of the aliphatic and aromatic series. When the base is mixed with the aldehyde, either alone or in alcoholic solution, a spon-

taneous rise of temperature takes place and the condensation-product formed crystallises out.

*Parabenzylideneamidodimethylaniline* or *benzylideneparadimethylphenylenediamine*,  $\text{CHPh} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , thus obtained from benzaldehyde and paramidodimethylaniline, forms pale-yellow glistening scales or needles which melt at  $93^\circ$ . It is soluble in ether and benzene and in boiling alcohol. It is a bivalent base and yields a *dihydrochloride*,  $\text{C}_{15}\text{H}_{16}\text{N}_2 \cdot 2\text{HCl}$ .

The author has obtained similar compounds with salicylaldehyde, cuminlaldehyde, anisaldehyde, &c., which will be described shortly, and he is also investigating the action of other unsymmetrical disubstituted diamines.

L. T. T.

### Condensation-products of the Derivatives of Salicylaldehyde.

By A. RÖSSING (*Ber.*, 17, 2988—3010). — *Orthaldehydophenoxyacetic acid*,  $\text{COH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$ , is prepared by gently fusing equivalent quantities of monochloroacetic acid and salicylaldehyde. The product is mixed with a sufficient quantity of sodium hydroxide solution (sp. gr. 1.2—1.3) to render it strongly alkaline, and heated on a water-bath with continual stirring until the mass thickens. It is then dissolved in hot water and the solution is acidified with hydrochloric acid, when the acid is deposited in crystalline plates or occasionally as an oil. The crystals melt at  $132^\circ$  and dissolve freely in alcohol, ether, and in hot water. The concentrated aqueous solution yields precipitates with magnesium sulphate, copper sulphate, silver nitrate, and lead acetate. It exhibits all the characteristic reactions of an aldehyde. The *ethylic* salt of the acid crystallises in needles melting at  $114^\circ$ , and is soluble in alcohol and ether. On the addition of bromine to a hot aqueous solution of aldehydophenoxyacetic acid, the monobromo-derivative,  $\text{C}_9\text{H}_7\text{BrO}_4$ , is deposited in silky needles melting at  $163^\circ$ ; it is soluble in alcohol, ether, and chloroform.

Aniline unites directly with aldehydophenoxyacetic acid to form the compound  $\text{NPh} \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$ . This substance is not attacked by ammonia, but it combines with acids to form salts. The *hydrochloride*,  $\text{C}_{15}\text{H}_{15}\text{NO}_4 \cdot \text{HCl}$ , crystallises in yellow needles, melts at  $190$ — $191^\circ$ , and is soluble in hot water and alcohol. The sulphate,  $\text{C}_{15}\text{H}_{15}\text{NO}_4 \cdot \text{H}_2\text{SO}_4$ , melts at  $186^\circ$ .

The acid also combines with phenylhydrazine, yielding the compound  $\text{N}_2\text{HPh} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$ . It is a red crystalline substance which begins to soften at  $60^\circ$  and melts completely at  $105^\circ$ . It dissolves freely in alcohol, ether, and in alkalis. When oxidised with potassium permanganate, aldehydophenoxyacetic acid yields *salicyloxyacetic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$ , a crystalline compound melting at  $187^\circ$ . The acid is soluble in alcohol, ether, and in hot water. Neutral solutions form precipitates with lead, copper, and silver salts. The latter,  $\text{C}_9\text{H}_6\text{Ag}_2\text{O}_6$ , is soluble in much water. The calcium, barium, strontium, potassium, and sodium salts of the acid are crystalline. They dissolve freely in water. *Diethylic salicyloxyacetate*,  $\text{C}_9\text{H}_6\text{O}_5\text{Et}_2$ , is an oily liquid which is decomposed by distillation. By the action of alcoholic ammonia at  $100^\circ$ , it is converted into the *diamide* melting at  $158^\circ$ .

*Orthocoumaroxyacetic acid*,  $\text{COOH} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$ , prepared by the action of acetic anhydride and anhydrous sodium acetate on aldehydophenoxyacetic acid, is deposited from a hot aqueous solution in needle-shaped crystals melting at  $190^\circ$ . The acid is soluble in alcohol, ether, and in hot water. Its lead, silver, and magnesium salts are either insoluble or sparingly soluble in water. The *dibromide* of coumaroxyacetic acid is a crystalline body; it melts at  $220^\circ$ , and is soluble in alcohol and ether. It is probably converted into propiophenoxyacetic acid,  $\text{COOH} \cdot \text{C} : \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$ , by the action of alcoholic potash.

If an excess of sodium acetate is used in the preparation of coumaroxyacetic acid, coumarone,  $\text{C}_6\text{H}_4 \langle \text{CH} \rangle_{\text{O}} \text{CH}$ , is formed. Coumaroxyacetic acid is converted into its anhydride,  $\text{C}_6\text{H}_4 \langle \text{CH} : \text{CH} \cdot \text{CO} \rangle_{\text{O} - \text{CH}_2 \cdot \text{CO}} \text{O}$ , when it is heated for a few minutes with a concentrated solution of phosphoric acid. The anhydride melts at  $176^\circ$ , and dissolves easily in alcohol and ether. It readily absorbs bromine-vapour, yielding the dibromide which crystallises in orange-coloured needles melting at  $213^\circ$ . A bluish-green amorphous substance of the composition  $\text{C}_9\text{H}_7\text{NO}_3$  is precipitated on the addition of water to a solution of the phenylhydrazine-derivative of aldehydophenoxyacetic acid in warm sulphuric acid. The precipitate dissolves in alkalis, forming a cherry-coloured solution, and in alcohol with a bluish-green coloration. The same compound is formed when equivalent quantities of orthoxybenzylidenephénylhydrazine and monochloroacetic acid are heated at  $100^\circ$ .

*Diacylorthoxybenzylidenephénylhydrazine*,  $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N}_2 \cdot \text{AcPh}$ , is deposited from alcoholic solutions in large prisms melting at  $133^\circ$ ; it is soluble in benzene, ether, chloroform, hot alcohol, and in hot hydrochloric acid. It is decomposed by distillation into acetic acid, phenol, acetanilide, and a reddish-yellow crystalline compound melting at  $113^\circ$ . The *dibromide*,  $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3\text{Br}_2$ , is an unstable crystalline compound. It is decomposed by boiling with alcohol, with elimination of hydrobromic and acetic acids. The solution on cooling deposits crystals of *monacetylxydibromobenzylidenephénylhydrazine*,  $\text{OAc} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH} : \text{N}_2 \cdot \text{HPh}$ ; this melts at  $188^\circ$  and dissolves in chloroform and benzene. It is decomposed by the action of hot hydrochloric acid, yielding phenylhydrazine hydrochloride. It is decomposed by alkalis, forming *hydroxydibromobenzylidenephénylhydrazine*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH} : \text{N}_2 \cdot \text{HPh}$ , a crystalline substance melting at  $148^\circ$ , soluble in alcohol, chloroform, benzene, ether, and dilute alkalis. *Diacylorthoxydibromobenzylidenephénylhydrazine*,  $\text{AcO} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH} : \text{N}_2 \cdot \text{AcPh}$ , prepared by heating the monacetic-derivative with acetic anhydride, crystallises in white needles which melt at  $158^\circ$ . The crystals dissolve freely in alcohol, ether, benzene, and chloroform. W. C. W.

**Terephthalophenone.** By NÖLTING and KOHN (*Bull. Soc. Chim.*, **42**, 339).—This compound,  $\text{C}_6\text{H}_4(\text{COPh})_2$  [1 : 4], is obtained by acting on benzene with terephthalyl chloride in presence of aluminium chloride. It is a white crystalline solid, insoluble in water, but soluble in alcohol and ether. The alcoholic solution is not attacked



by alkalis. From these properties, the compound appears to have the constitution of a diacetone, such as Ador's isophthalophenone, and not that of a lactone like the phthalophenone of Friedel and Crafts.

W. R. D.

**Quinones.** By NÖLTING and BAUMANN (*Bull. Soc. Chim.*, **24**, 341).—Quinones are obtained by distilling solutions of the sulphates of various bases with chromic acid. Mesidine yields meta-xyloquinone; crystallised cumidine yields para-xyloquinone; unsymmetrical meta-xylidine yields toluquinone in small quantity, and metatoluidine the same quinone in large quantity.

W. R. D.

**Derivatives of Azocumic Acid.** By P. ALEXÉEFF (*Bull. Soc. Chim.*, **42**, 321).—Azocumic acid is prepared by acting with sodium amalgam on nitrocumic acid. It forms ruby-red crystals having a sp. gr. of about 9.24, and melts with decomposition at 280°. The crystals dissolve in alcohol, and to a less extent in ether and chloroform, but are insoluble in benzene, light petroleum, and water. Concentrated sulphuric acid dissolves them, and when the red liquid is heated and precipitated with water, a brown flocculent substance falls, leaving a blue liquid. Nitric acid also dissolves azocumic acid to a cherry-red liquid, which becomes green when it is diluted with water. If previously heated and ammonia then added, a yellowish-red liquid with a fine green fluorescence is obtained. The action of potassium permanganate on an alkaline solution gives rise to *azoxyisopropylbenzoic acid*. By the action of powdered zinc or sodium amalgam on an alkaline solution of the acid, it is decolorised, with formation of *hydrazocumic acid*. The metallic and ethereal salts of azocumic acid were also prepared.

W. R. D.

**Melilotic Acid and Anhydride.** By H. HOCHSTETTER (*Annalen*, **226**, 355—363).—An aqueous solution of melilotic acid is partly converted into the anhydride by boiling. The anhydride combines with water very slowly at the ordinary temperature. It does not dissolve readily in a hot concentrated solution of potassium carbonate. Melilotic acid is completely converted into the anhydride by the action of hydrobromic acid at the ordinary temperature. It is probable that orthobromhydrocinnamic acid is first formed, which afterwards decomposes into hydrogen bromide and melilotic anhydride.

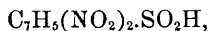
Melilotic anhydride is converted into coumarin by the action of bromine-vapour at 170°. At the ordinary temperature, bromine acts on a solution of the anhydride in carbon bisulphide, forming monobromomelilotic anhydride,  $C_9H_7BrO_2$ . This compound is deposited from its solution in chloroform in colourless prisms, which melt at 106°, and do not decompose at 180°. Boiling water slowly converts it into bromomelilotic acid,  $C_9H_7BrO_3$ . This acid crystallises in rectangular plates soluble in alcohol and in warm chloroform. It melts at 141—142° with decomposition into water and the anhydride.

W. C. W.

**Action of Hydrobromic Acid and Bromine on Coumarin, Coumarone, and Orthocoumaric Acid.** By G. EBERT (*Annalen*, **226**, 347—355; comp. Abstr., 1883, 471).—When hydrogen bromide is passed into a solution of coumarin in strong hydrobromic acid, crystals melting at  $42^{\circ}$  are deposited, which rapidly decompose into hydrogen bromide and coumarin. Coumarin dibromide is decomposed by boiling with water; it splits up into coumarin and free bromine. The latter acts on the coumarin and on the dibromide, yielding  $\alpha$ -dibromocoumarin and  $\beta$ -bromocoumarin, which have been previously described by Perkin (this Journal, 1870, 368; 1871, 37).

To convert coumarin into coumaric acid, 10 grams of coumarin are added to a solution of 3.5 grams sodium in 60 c.c. absolute alcohol. The mixture is boiled for  $1\frac{1}{2}$  hours in a flask provided with a reflux condenser. It is then diluted with water, the alcohol distilled off, and the acid precipitated from the residue by hydrochloric acid. Coumaric acid is converted into coumarin by the action of hydrobromic acid at  $0^{\circ}$ . Bromine slowly acts on coumaric acid dissolved in carbon bisulphide, forming  $\beta$ -dibromocoumarin. *Monobromocoumarone*,  $C_9H_7BrO$ , is formed by the action of alcoholic potash on the dibromide. It crystallises from alcohol in colourless needles which are soluble in water, and melt at  $36^{\circ}$ . W. C. W.

**Thiosulphonic Acids and Sulphinic Acids of Toluene.** By J. PERL (*Chem. Centr.*, 1884, 468).—*Diamidotolueneparathiosulphonic acid*,  $C_7H_5(NH_2)_2.SO_2SH$ , is obtained by acting with ammonium sulphide on dinitrotolueneparasulphonic chloride, and decomposing the resulting ammonium salt by hydrochloric or glacial acetic acid. It crystallises in silky needles, and decomposes at  $152^{\circ}$ . By the action of acids, it is converted into the *sulphinic acid*,  $C_7H_5(NH_2)_2.SO_2H$ , with separation of sulphur. *Diamidotolueneparasulphinic acid* is converted by nitrous acid into a voluminous brick-red compound, which is apparently the corresponding diazo-derivative. When dinitrotoluenesulphonic chloride is acted on by zinc-dust, the product treated with barium hydroxide, and the barium salt obtained decomposed by means of sulphuric acid, *dinitrotolueneparasulphinic acid*,



is obtained, and may be converted into *diamidotolueneparathiosulphonic acid* by the action of ammonium sulphide.

When disulphanilic acid is submitted to the action of potassium permanganate, the *azotetrasulphonate*,  $C_6H_3(SO_3K)_2.N_2.C_6H_3(SO_3K)_2$ , is produced, and crystallises with 3 mols.  $H_2O$ . The free acid has not been obtained, as the addition of an acid throws down a sparingly soluble hydrogen potassium salt. The chloride melts at  $91^{\circ}$ , and the amide at  $229-230^{\circ}$ . A. K. M.

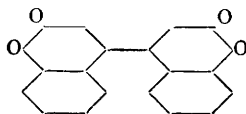
**Phenylhydrazine-derivatives of  $\alpha$ - and  $\beta$ -Naphthaquinone. Identity of the  $\alpha$ -Derivative with Benzeneazo- $\alpha$ -naphthol.** By T. ZINCKE and H. BINDEWALD (*Ber.*, **17**, 3026—3033).— *$\alpha$ -Naphthaquinonehydrazide* is precipitated when an aqueous solution of phenylhydrazine hydrochloride is added to a solution of  $\alpha$ -naphthaquinone in

glacial acetic acid. It is purified by solution in baryta-water, precipitation by hydrochloric acid, and recrystallisation from alcohol.  $\alpha$ -Naphthaquinonehydrazide is identical with benzeneazo- $\alpha$ -naphthol.  $\beta$ -Naphthaquinonehydrazide melts at  $138^\circ$ , and closely resembles but is not identical with benzeneazo- $\beta$ -naphthol. It neither combines with acids nor bases, but it unites with bromine, forming a crystalline dibromide,  $C_{16}H_{10}Br_2N_2O$ , melting between  $215^\circ$  and  $219^\circ$ . The authors suggest the following formulæ for these substances:—Benzeneazo- $\beta$ -naphthol,



$\beta$ -naphthaquinonehydrazide  $[O : N_2HPh = 1 : 2]$ . W. C. W.

**Dinaphthylidiquinone.** By O. KORN (*Ber.*, 17, 3019—3026).—The dinaphthylidiquinone of Stenhouse and Groves (*Trans.*, 1878, 418) yields Lössen's  $\alpha\alpha$ -dinaphthyl (*Annalen*, 144, 27) when it is heated with zinc-dust, and Ador's diphthalic acid (*this Journal*, 1873, 67) on oxidation with potassium permanganate. Hence it follows that the constitution of the diquinone may be represented as



Dinaphthylidiquinone unites with aniline, forming a *tetranilide*,  $C_{20}H_8(NHPh)_2O_2(NPh)_2$ , crystallising in glistening metallic plates of a dark red colour. The crystals dissolve in glacial acetic acid, but are insoluble in the ordinary solvents; they melt at  $248$ — $250^\circ$ . The *hydrochloride*,  $C_{44}H_{30}N_4O_2(HCl)_2$ , is freely soluble in alcohol and sparingly soluble in water. In the preparation of the tetranilide, Zincke's  $\beta$ -naphthaquinonedianilide (*Abstr.*, 1882, 967) is obtained as a by-product.

In order to distinguish between (1)  $\alpha$ -naphthaquinol, (2)  $\beta$ -naphthaquinol, and (3)  $\beta$ -dinaphthylidiquinol, the author acts on them with nitric acid of sp. gr. 1.48, when they are converted into (1)  $\alpha$ -naphthaquinone, (2) nitro- $\beta$ -naphthaquinone, and (3)  $\beta$ -dinaphthylidiquinone, or they may be converted into their acetic derivatives: (1) diacetyl- $\alpha$ -naphthaquinol, forms transparent plates melting at  $129^\circ$ , (2) tetracetyl- $\beta$ -dinaphthylidiquinol, silky needles which melt with decomposition at  $166^\circ$ , (3) diacetyl- $\beta$ -naphthaquinol, transparent plates melting at  $105^\circ$ .

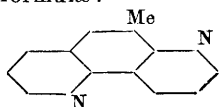
Liebermann's  $\alpha$ -dinaphthylidiquinol yields  $\beta\beta$ -dinaphthyl on distillation with zinc-dust. W. C. W.

**Methylphenanthroline.** By Z. H. SKRAUP and O. W. FISCHER (*Monatsh. Chem.*, 5, 523—530).—By heating nitrobenzene and toluylenediamine  $[CH_3 : NH_2 : NH_2 = 1 : 2 : 4]$  together with sulphuric acid and glycerol, a base is obtained which the authors style *methylphenanthroline*. This compound is obtained from the product of the reaction by treating it first with caustic soda and subsequently dissolving the resinous mass so obtained in hydrochloric acid. From

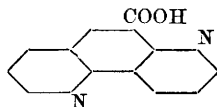
this solution, alcohol precipitates the hydrochloride. The hydrochloride is next converted into the chromate, from which the pure base is obtained. It melts at  $95-96^{\circ}$ , boils at a temperature above  $360^{\circ}$ , and resembles phenanthroline in its general characters (Abstr., 1883, 86). It unites with water to form a crystalline compound having the formula  $C_{13}H_{10}N_2 + 5H_2O$ . The *hydrochloride*,  $C_{13}H_{10}N_2 \cdot HCl + 4H_2O$ , is easily soluble in water, and crystallises from dilute alcohol in long transparent needles. The *chromate*,  $(C_{13}H_{10}N_2)_2 \cdot H_2Cr_2O_7$ , forms yellow needle-shaped crystals, which are sparingly soluble in water. The *platinochloride*,  $C_{13}H_{10}N_2 \cdot H_2PtCl_6 + 2H_2O$ , is obtained as a light yellow crystalline precipitate. The compound of the base with picric acid is obtained as a crystalline precipitate sparingly soluble in boiling alcohol, and melting at  $253^{\circ}$ .

*Phenanthrolinecarboxylic acid*,  $C_{13}H_8N_2O_2$ , is obtained by oxidising methylphenanthroline with chromic acid. It melts at  $277^{\circ}$ , is almost insoluble in hot water, and sparingly soluble in alcohol and acetic acid, but is dissolved alike by alkalis and by mineral acids.

The calcium salt crystallises in opaque needles having the formula  $2[(C_{13}H_7N_2O_2)_2Ca + 5H_2O] + C_{13}H_8N_2O_2$ , and on distillation yields phenanthroline. The formation of phenanthroline from this acid, and the production of methylphenanthroline from toluylenediamine, show that the constitution of these compounds may be expressed by the following formulæ:—



Methylphenanthroline.



Phenanthrolinecarboxylic acid.

P. P. B.

**New Method of Preparing Phenanthroline.** By Z. H. SKRAUP (*Monatsh. Chem.*, 5, 531—533).—As  $\beta$ -amidoquinoline yields phenanthroline when heated with nitrobenzene, glycerol, and sulphuric acid, its amido-group probably occupies the position 4.

P. P. B.

**Constitution of Terebic and Teraconic Acids.** By B. FROST (*Annalen*, 226, 363—376).—*Ethyl teraconate*,  $C_8H_8(COOEt)_2$ , prepared by saturating an alcoholic solution of teraconic acid with hydrogen chloride, is a colourless liquid boiling at  $254^{\circ}$ . Teraconic acid is not acted on by nascent hydrogen, but it is converted into terebic acid by the action of hydrobromic acid, or of hot hydrochloric or sulphuric acid. Monobromoterebic acid is produced when bromine is added to the aqueous or ethereal solution of teraconic acid. Monobromoterebic acid forms colourless crystals which melt at  $151^{\circ}$  with decomposition. It is soluble in ether, but is decomposed by hot water, yielding terebic acid. A chloroterebic acid is formed when chlorine acts on teraconic acid in presence of water, but this substitution-product is not identical with the chloroterebic acid described by Williams (this Journal, 1874, 70) and by Roser (Abstr., 1884, 459). It forms rhombic prisms  $a : b : c = 0.9827 : 1 : 0.7137$ . The acid melts at  $168^{\circ}$  with decomposition, and is easily decomposed by water,

yielding terebilic acid,  $C_7H_8O_4$ . Nascent hydrogen from sodium amalgam converts terebilic into terebic acid. Terebilic acid slowly decomposes at 250—255, forming a crystalline lactone which melts at 8° and boils at 207°. It is probably identical with the terelactone which Geisler (Abstr., 1882, 41) obtained from dibromocaproic acid.

When terebic acid is heated in sealed tubes at 160° with a large excess of baryta-water, it splits up into succinic acid and acetone. This reaction can only be explained on the assumption that terebic acid has the constitution  $COOH.CH<\overset{-CH_2-}{CMe_2O}>CO$ . Terebilic acid will then be represented by  $COOH.C<\overset{CH-}{CMe_2O}>CO$ .

W. C. W.

**Wood-oil from Cochin China.** J. LÉON-SOUBETRAU (*J. Pharm.* [5], 10, 251—254).—The oil is yielded by several trees of the family Dipterocarpus. The method of extraction is described. On standing, two layers form, a clear upper one somewhat fluorescent, and a lower one thicker and darker. The density of these oleo-resins is about 0.96—0.966. The light oil mixed with water and distilled yields about 30 per cent. of an oily distillate; distillation commences at 242° and may be continued up to 295° in the case of both oils. Fuming nitric acid acts very violently on the oil; nitric acid gives a violet coloration, sulphuric acid a red, and hydrochloric acid a reddish-violet with it. Iodine also has an energetic action. It is used as a varnish and lacquer and also as a substitute for copaiva. H. B.

**Eucalyptole.** By E. JAHNS (*Ber.*, 17, 2941—2944).—The author has investigated the oil obtained by distilling the fresh leaves of *Eucalyptus globulus*. On rectification, the principal portion of this oil distilled between 170—180°, the remainder consisting of high-boiling terpenes and traces of a phenolic compound. The portion boiling at 170—180° still contained terpenes together with an oxygenated compound. This latter was isolated by the help of its hydrochloric acid compound, as recommended for cyneole by Wallach and Brass (this vol., p. 171). Thus purified *eucalyptole* has the formula  $C_{10}H_{18}O$ . It boils at 176—177° (column in vapour), has a sp. gr. of 0.923 at 0°, and is optically inactive. The authors find that this substance is identical with cyneole and the chief constituent of oil of cajeput (see Wallach, "Ethereal Oils," this vol., p. 171). They believe that the *eucalyptole* obtained by Clôez (*Compt. rend.*, 1870, 70, 687) to which he ascribed the formula  $C_{12}H_{20}O$ , still contained terpenes, whilst that described by Faust and Homeyer (*Ber.*, 7, 63) as being free from oxygen was probably obtained from another species of *Eucalyptus*.

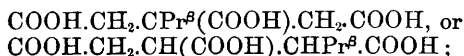
L. T. T.

**Stearopten from Essence of Patchouli.** By H. C. C. MAISCH (*J. Pharm.* [5], 10, 223—224, from *Amer. J. of Pharm.*, 1884).—This camphor is purified by solution in alcohol and then in ether, from which last it crystallises in hexagonal prisms. It melts at 55—56°, and has a vapour-density of 8.00 at 324°. Heated with zinc chloride, it loses one molecule of water and leaves a hydrocarbon,  $C_{15}H_{24}$  or  $C_{15}H_{26}$ .

H. B.

**Camphoronic Acid.** By J. BREDT (*Annalen*, **226**, 249—261).—The properties of camphoronic acid have been investigated by Kachler (*Ann.*, **159**, 281) Kissling, Neugebauer, and Hjelt (*Abstr.*, 1880, 669), who regard the substance as a lactic acid. The author obtained the acid from the mother-liquors from the preparation of camphoric acid, by precipitation as a barium salt. This salt is decomposed by hydrochloric acid, the mixture evaporated to dryness and the residue extracted with ether to dissolve out the camphoric acid. After removing the ether, the aqueous solution of the acid is nearly neutralised with milk of lime, and heated at  $100^{\circ}$ , when the pure calcium salt,  $\text{Ca}_3(\text{C}_9\text{H}_{11}\text{O}_6)_2 + 12\text{H}_2\text{O}$ , is deposited. The author's results differ in several respects from those of his predecessors. The barium salt,  $\text{Ba}_3(\text{C}_9\text{H}_{11}\text{O}_6)_2$ , is anhydrous and the silver salt,  $\text{C}_9\text{H}_{11}\text{O}_6\text{Ag}$ , crystallises with 1 mol.  $\text{H}_2\text{O}$ . *Triethyl camphoronate*,  $\text{C}_9\text{H}_{11}\text{O}_6\text{Et}_3$ , formed by the action of ethyl iodide on the *anhydrous* silver salt, boils at  $301^{\circ}$ . The *diethyl* salt, which has been described by Kachler, is decomposed by distillation into alcohol and the monoethylic salt of anhydrocamphoronic acid.

The author regards camphoronic acid as isopropyltricarballic acid, and gives his preference to the first of the following formulæ:



he regards camphor as having the constitution

$$\begin{array}{c} \text{CH}_2 \cdot \text{CPr}^s \cdot \text{CH}_2 \\ | \quad | \quad | \\ \text{CH}_2 \cdot \text{CMe} \cdot \text{CO} \end{array}.$$

W. C. W.

**Existence of Glycyrrhizin in several Vegetable Families.** By E. GUIGNET (*Compt. rend.*, **100**, 151—153).—Glycyrrhizin exists not only in several species of Leguminosæ, but also in some plants of perfectly distinct families; for example, it occurs in large quantity in the rhizomes of *Polypodium vulgare*, which grows abundantly in the neighbourhoods of Paris and Brest, and in the Vosges, also in the rhizomes of *P. semipennatifidum*, var. *indursum*, which grows on the temperate regions of the Andes. Both these plants are used as substitutes for liquorice.

The best method of extracting glycyrrhizin is to treat the dried and powdered plant with acetic acid of  $8^{\circ}$ , mix the solution with alcohol, filter, evaporate the filtrate to a syrup, and add water, which dissolves out ammonium acetate and other impurities but leaves the glycyrrhizin undissolved.

The paper concludes with a summary of the chemical history of glycyrrhizin. C. H. B.

**Glucoside from Strychnos Nux-Vomica.** By W. R. DUNSTAN and F. W. SHORT (*Pharm. J. Trans.* [3], **14**, 1025—1026).—By percolating the dried pulp of the fruit of *Strychnos nux-vomica* with a mixture of chloroform and alcohol, by the method already described (*Abstr.*, 1883, 689), 4 and 5 per cent. of a crystalline substance is obtained. It forms colourless prismatic crystals, softening at  $200^{\circ}$ , melting

at 215°, readily soluble in water and alcohol, less so in ether, chloroform, and benzene. Its aqueous solution is not precipitated by alkaloid reagents, nor by lead acetate or silver nitrate, neither is it affected by ferric chloride. It gives no colour reaction with nitric acid or oxidising agents; it, however, decolorises bromine solution, and is oxidised by chromic mixture. Warmed with sulphuric acid, it gives a fine red colour, changing to deep purple. It is a glucoside, termed *loganin*; and when treated in the usual way yields glucose and a substance, *loganetin*, with similar properties to those described above. The *Strychnos nux-vomica* seeds also contain a small quantity of this glucoside.

D. A. L.

**Crystalline Substance from Jambosa Root.** By A. W. GERRARD (*Pharm. J. Trans.* [3], 14, 717—718).—The root of *Myrtus Jambosa*, L., yields a neutral crystalline substance, an acid, a resin, and a minute quantity of an alkaloïd. The crystalline substance, *jambosin*,  $C_{10}H_5NO_3$ , melts at 77°, resolidifies at 60°, is white and tasteless, soluble in cold ether, alcohol, chloroform, in hot light petroleum and in boiling water; insoluble in cold water. With strong sulphuric acid, it gives a bright green colour soon changing to reddish-brown; with nitric acid a violent action ensues, nitrous fumes are evolved, and an orange-coloured liquid is produced, in which water forms a precipitate. It is neither a glucoside nor an acid.

D. A. L.

**Chebulinic Acid.** By FRIDOLIN (*Chem. Centr.*, 1884, 641).—The author has isolated from the fruit of *Terminalia chebula* an acid which he proposes to call *chebulinic acid*. Its percentage composition approaches that of gallic acid, and in some of its properties it resembles that acid, whilst in others it is essentially different. It crystallises in rhombic prisms, has a sweetish taste, is soluble in alcohol and hot water, but only sparingly in cold water. It reduces Fehling's solution, and gives a blue-black precipitate with ferric chloride. In a very dilute solution of the latter, it gives a green tint (gallic acid gives a light brown). Potassium cyanide produces no effect, whilst with gallic acid it strikes a deep rose tint.

R. R.

**Pipitzahoic Acid.** By T. GREENISH (*Pharm. J. Trans.* [3], 14, 698—700).—Microscopical examination proves that pipitzahoic acid exists as a true secretion in the roots of *Perezia fruticosa*. The root also contains inulin.

D. A. L.

**Colouring Matters of Ebony Wood.** By A. BELOHOUBEK (*Chem. Centr.*, 1884, 566).—The author considers that the colouring matters of ebony wood are due to a reducing action excited in originally colourless substances, and carried so far as the separation of carbon, as one colouring matter is insoluble in alkalis, and completely combustible, yielding only carbonic anhydride. Another colouring matter, however, is readily soluble in alkalis, and this the author believes to be humic acid.

R. R.

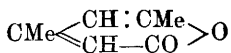
**Decomposition-products of Pyridine Derivatives.** By A. HANTZSCH (*Ber.*, 17, 2903—2921).—This is a continuation of the author's previous work (*Abstr.*, 1884, 1045) on this subject. When methylpseudolutidostyryl hydrochloride is strongly heated in a current of hydrogen chloride, the methyl-group attached to the nitrogen-atom is replaced by hydrogen, and *pseudolutidostyryl*,  $C_7H_5ON$ , is formed. This compound crystallises in needles, melts at  $180^\circ$ , and boils at  $303\text{--}305^\circ$ . It is soluble in water, alcohol, and ether. It combines both with acids and with bases. The *potassium* compound crystallises in silvery scales, the *hydrochloride* in prisms, the *platinochloride* in brownish anhydrous prisms. When this base is treated with sodium ethylate and excess of methyl iodide, methylpseudolutidostyryl is re-formed. It is thus clear that no rearrangement of the molecule can have taken place during the formation of pseudolutidostyryl, but simply a replacement of methyl by hydrogen. The formula of this compound is therefore  $CMe \begin{smallmatrix} \text{CH} : CMe \\ \text{CH} - CO \end{smallmatrix} > NH$ . When the hydrochloride is mixed with ten times its weight of zinc-dust and quickly heated in a current of hydrogen, a *lutidine*,  $CMe \begin{smallmatrix} \text{CH} : CMe \\ \text{CH} . CH \end{smallmatrix} > N$ , distils over. This compound boils at  $154\text{--}155^\circ$ , and shows all the characteristics of a homologue of pyridine. It dissolves freely in cold water, but is entirely reprecipitated on boiling. The *platinochloride* crystallises in dark orange-coloured plates which are anhydrous and melt at  $216\text{--}217^\circ$ . The other salts are not very characteristic. The *aurochloride* crystallises with difficulty; the *hydrochloride* and *hydrobromide* crystallise in needles; the *picrate* forms bright yellow needles which melt at  $176\text{--}179^\circ$ . The dimethylpyridines hitherto obtained resemble this compound in properties, but have probably all been mixtures of isomerides. The author believes this lutidine to be the first pure dimethylpyridine which has been obtained.

In order to elucidate the decomposition of ethyl collidinedicarboxylate methiodide described in his last paper (*loc. cit.*), the author prepared *ethyl phenyllutidinedicarboxylate*,  $C_5NPhMe_2(COOEt)_2$ , by the action of ammoniobenzaldehyde on ethyl acetoacetate. This compound, however, is no longer capable of combining with methyl iodide. It was therefore converted into *hydrogen ethyl phenyllutidinedicarboxylate* by digestion with rather less than one molecular proportion of alcoholic potash. This acid salt crystallises in cubes melting at  $179\text{--}180^\circ$ , and is easily soluble in boiling alcohol, sparingly so in cold alcohol or ether. It forms neutral metallic salts. When subjected to distillation, carbonic anhydride is evolved, and *ethyl phenyllutidinedicarboxylate*,  $C_5NHPhMe_2.COOEt$ , formed. This compound is a thick liquid which boils at  $316\text{--}320^\circ$ . It dissolves in acids, but its salts do not crystallise well; the *platinochloride* melts at  $196^\circ$ . *Phenyllutidinedicarboxylic acid*,  $C_5NHPhMe_2.COOH$ , crystallises with 2 mols.  $H_2O$ , which it loses at  $120\text{--}130^\circ$ , and then melts at  $189\text{--}190^\circ$ . Its salts are described; the *platinochloride* crystallises in orange prisms with 1 mol.  $H_2O$ , which it loses at  $110\text{--}115^\circ$ .

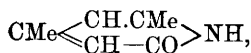
Ethyl phenyllutidinedicarboxylate was then converted into *ethyl*



*phenyllutidinecarboxylate methiodide* by digestion, at  $100^{\circ}$ , with its own weight of methyl iodide. The methiodide is sparingly soluble in cold water and alcohol, and crystallises in needles which melt at  $205\text{--}206^{\circ}$ . When treated with potassium hydroxide, this compound undergoes a decomposition similar to that already described (*loc. cit.*) for the collidine-derivative. *Methylcarbophenyllutidylumdehydride*,  $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}$ , thus obtained crystallises from benzene in rhombic plates, which sometimes contain 1 mol.  $\text{C}_6\text{H}_6$ , sometimes are free from benzene; it melts at  $160\text{--}161^{\circ}$ . It is easily soluble in benzene and alcohol, sparingly in boiling water or ether. It is decomposed when heated, and none of its salts could be isolated. Fuming hydrochloric acid at  $170\text{--}180^{\circ}$  converts it into a *methylated pseudostyryl* of *phenylpicoline*,  $\text{CPh} \begin{smallmatrix} \text{CH} : \text{CMe} \\ \text{CH} - \text{CO} \end{smallmatrix} \text{NMe}$ , acetic acid being formed at the same time. This pseudostyryl is easily soluble in alcohol, less so in benzene, very sparingly in ether, and melts at  $112^{\circ}$ . It is not volatile with steam, but dissolves pretty freely in boiling water. Its reaction is neutral, but it yields well crystallised salts, which are, however, decomposed by water; the platinochloride forms light yellow microscopic needles containing  $3\text{H}_2\text{O}$ . In the formation of this pseudostyryl, the acetic acid produced must be derived from the ethyl acetoacetate employed in the formation of the carboxylic ether. Judging from analogy, it is clear that in the collidine compound previously described the acetic acid was derived from the same source, and not from the aldehyde. The author believes the formation of these dehydrides to be a general reaction with similar pyridine derivatives obtained by the condensation of aldehydes with acetoacetic acid. Mesitene-lactone, already described by the author, stands in close relationship to these compounds,



Mesitene-lactone.



Pseudolutidostyryl (mesitene-lactam).

but all attempts to convert the lactone into the styryl by the action of ammonia proved futile.

When oxidised by permanganate, 1 molecule of methylpseudolutidostyryl requires 4 mols. of permanganate. Acetic acid, carbonic anhydride and two nitrogenous acids are produced. One of these acids proved to be methyloxamic acid,  $\text{NHMe.CO.COOH}$ , whilst the other could only be obtained as an impure syrup. When boiled with excess of baryta or alkali this syrupy acid yields methylamine, and must, therefore, contain the  $(\text{CO.NHMe})$  group.

The author now finds the melting point of pure methylpseudolutidostyryl to be  $90\text{--}92^{\circ}$ , and not  $70^{\circ}$ , as given in his previous communication.

L. T. T.

**Thallin Preparations.** By G. VULPIUS (*Arch. Pharm.* [3], 22, 840—845).—Thallin is a new name for tetrahydroparaquinanisoil, a derivative of paraquinanisoil. The sulphate and tartrate of thallin have been investigated clinically. Paraquinanisoil is produced by heating paramidoanisoil with parabromanisoil, glycerol, and sulphuric

acid at 140—155°, as an oily liquid which, with hydrochloric acid, gives a salt soluble in water. Thallin sulphate and tartrate occur usually in the form of a nearly white crystalline powder, although larger crystals can be easily obtained. The salts melt at 100° with slight browning. The sulphate is soluble in five times its weight of cold water, and very soluble in boiling water. The aqueous solution readily turns brown on exposure to light. It is soluble in about 100 parts alcohol; this solution also darkens; the coloration appears, however, to be mainly due to impurities. The solutions of the tartrate are much less sensitive to light. The sulphate is almost insoluble in ether, but somewhat more soluble in chloroform. The tartrate is much less soluble in all the above vehicles than is the sulphate. The sulphate gives the following reactions:—A solution of 1 : 10,000, after a few seconds, gives a deep emerald-green liquid with a few drops of ferric chloride; the colour is not changed by the addition of a few drops of concentrated sulphuric acid. Reducing agents change the colour: thus sodium thiosulphate changes it to violet, then to wine-red; oxalic acid changes it into light yellow, which becomes saffron-yellow on heating. Other oxidising agents produce the green colour when carefully added, but the reaction is not so sensitive as with ferric chloride. Picric acid gives a yellow precipitate. Tannin, mercuric chloride, stannous chloride, dilute nitric acid, and hydrochloric acid produce no change in the solution. Thallin sulphate in contact with concentrated sulphuric acid shows no change in the cold; on warming, it gives a brownish coloration. Vapour of fuming nitric acid colours the dry sulphate carmine-red; the colour gradually changes to brown. Thallin solution gives with fuming nitric acid, when warmed, a deep red colour, taken up by chloroform. Caustic alkalis and ammonia give a white turbidity in moderately concentrated solutions; the turbidity disappears on adding water, alcohol, or ether.

J. T.

**Diquinolines.** By O. W. FISCHER (*Monatsh. Chem.*, 5, 417—425).—By the aid of Skraup's reaction (Abstr., 1881, 288 and 920), the author has obtained from benzidine [ $\text{NH}_2 : \text{NH}_2 = 4 : 4'$ ] a *diquinoline*,  $\text{C}_{18}\text{H}_{12}\text{N}_2$ , identical with that described by Weidel (Abstr., 1882, 69). From its method of formation, this must have the two quinoline-groups united at the 4 : 4 positions on the benzene-rings. The author's description of the salts of this base confirm the observations of Weidel, except in the case of the sulphates, of which two are described, namely, the *acid sulphate*,  $\text{C}_{18}\text{H}_{12}\text{N}_2 \cdot 2\text{H}_2\text{SO}_4$ , which crystallises in bundles of long needles, and is decomposed by water; and the *normal sulphate*,  $\text{C}_{18}\text{H}_{12}\text{N}_2 \cdot \text{H}_2\text{SO}_4 + 3\text{H}_2\text{O}$ , obtained by adding sulphuric acid to an alcoholic solution of the base; it is decomposed by water, and turns brown on exposure to the air. The base combines directly with methyl iodide, yielding the methiodide  $\text{C}_{18}\text{H}_{12}\text{N}_2 \cdot \text{MeI}$ ; this forms light-yellow crystals; when heated with an excess of methyl iodide, the compound  $\text{C}_{18}\text{H}_{12}\text{N}_2 \cdot 2\text{MeI}$  is formed, which melts above 290°.

Attempts made to prepare a diquinoline by passing quinoline through red-hot tubes did not yield satisfactory results. P. P. B.

**Nitroparatoluquinoline.** By E. FOURNEAUX (*Bull. Soc. Chem.* **42**, 337).—This substance is obtained by nitrating paratoluquinoline, dissolved in sulphuric acid, with the theoretical quantity of nitric acid. It crystallises from light petroleum in white needles, and melts at 116—116·5°. The platinochloride crystallises from water in yellow needles. On reduction, nitroparatoluquinoline yields *amidoparatoluquinoline*, crystallising in yellow needles, which melt at 132—133°; it is dissolved by the ordinary solvents and is very soluble in toluene. A nitroparatoluquinoline identical with the preceding compound is obtained when metanitroparatoluidine (m. p. 114°) is heated with glycerol, nitrobenzene, and sulphuric acid. This synthesis determines the constitution of these derivatives, and assigns to nitroparatoluquinoline the formula  $C_9NH_6Me.NO_2$  [ $NO_2 : Me = 1 : 4$ ].

W. R. D.

**Flavaniline.** By O. FISCHER and E. TÄUBER (*Ber.*, **17**, 2925—2928).—Picolinetricarboxylic acid, already shortly described (*Abstr.*, 1884, 600), melts at 232°, and decomposes at 236°. It is identical with the acid recently obtained from collidinedicarboxylic acid by R. Michael (this vol., p. 62), and when oxidised yields pyridinetetracarboxylic acid, as shown by that investigator. The latter acid may be obtained directly from flavenol by oxidation with 11 molecular proportions of permanganate in 5 per cent. aqueous solution. Towards the end of the oxidation, the action takes place exceedingly slowly, and the mixture requires to be heated on the water-bath for some days. Pyridinetetracarboxylic acid crystallises in needles containing water, which it only loses by long continued heating at 115°. The hydrated acid melts at 187°, the anhydrous, with decomposition and evolution of carbonic anhydride, at 227°. Michael gives the melting point as 188°, so that probably his specimen was not dehydrated. Several metallic salts are described.

It is thus clear that flavoline is phenyllepidine, and flavaniline and flavenol the amide and hydroxide respectively of flavoline, and that the last two have the constitutions  $C_6H_4(NH_2)Me = 2' : 4'$  and  $C_6H_4(OH)Me = 2' : 4'$  respectively.

L. T. T.

**Quinoline Dyes.** By W. SPALTEHOLZ (*Chem. Centr.*, 1884, 472).—The author made unsuccessful attempts to prepare the red dye formed according to Williams, by the action of tar quinoline and amyl iodide, the product being digested with aqueous potash. An attempt to obtain it by the method suggested by Hofmann (*Jahresh.*, 1862, 361) also yielded negative results. Amyl iodide and quinoline were heated together on a water-bath, and quinoline amyliodide,  $C_9NH_7.C_5H_{11}I$ , obtained; on warming this with an excess of potash, a reddish resinous mass is produced, readily soluble in alcohol with reddish-violet colour; the yield, however, is very small. A red colouring matter is also formed in small quantity by the action of alkalis on methyl- or ethylquinoline iodide. When ethylquinolineammonium iodide, prepared from quinoline (from the chromate), boiling at 232·5—233·5°, and ethyl iodide, is treated with aqueous alkali, a minute quantity of a dye is produced, but if quinoline (boiling at 231·5° at 753·5 mm.), obtained from the pure crystallised ethiodide be employed, no dye is

formed. A dye can, however, be obtained from crude quinoline and ethyl iodide. It crystallises in magnificent, iridescent, rhombic prisms or plates; its solutions are decolorised by acids, whilst alkalis precipitate the dye in amorphous flakes. This dye appears to be a condensation-product from 1 mol. quinoline ethiodide and 1 mol. quinaldine ethiodide, a compound of the same composition being produced by the action of potash on a mixture of these two substances. When dried at  $105^{\circ}$ , its composition is  $C_{23}H_{25}N_2I + \frac{1}{2}H_2O$ , but when dried at  $120^{\circ}$  it becomes anhydrous. From the above, it is concluded that purified quinoline from coal-tar is identical with artificial quinoline.

A. K. M.

**Conhydrine Derivatives.** By A. W. HOFMANN (*Ber.*, **18**, 5—23). The author has already shown (*Abstr.*, 1883, 220) that the product obtained by Werthheim (*Annalen*, **127**, 75) by the action of phosphoric anhydride or of hydrochloric acid on conhydrine is not conine, but a mixture of two less hydrogenised bases. He has now investigated this product more closely, and finds that it consists of two isomeric bases of the formula  $C_8H_{15}N$ , to which he gives the names  $\alpha$ - and  $\beta$ -coniceïne.

The decomposition of the conhydrine was effected by heating it with about four times its weight of fuming hydrochloric acid at  $220^{\circ}$  for four hours. The basic product boiled between  $155$ — $175^{\circ}$ , and yielded two crystalline hydrochlorides, one of which was deliquescent and the other not. The separation of the two bases was effected by means of their picrates.

$\alpha$ -Coniceïne,  $C_8H_{15}N$ , obtained from the sparingly soluble part of the above picrate, is a colourless liquid which boils at  $158^{\circ}$ , and has an odour resembling conine. It is sparingly soluble in water, and does not change on exposure to the air. It forms a *hydrochloride* which crystallises in deliquescent hexagonal plates. Its *picrate* crystallises in yellow needles which melt at  $225^{\circ}$ , and is sparingly soluble in cold alcohol, almost insoluble in water. It forms a sparingly soluble compound with mercuric chloride. Its *platinochloride* crystallises in yellow rhombic prisms, easily soluble in water. Its *aurochloride* forms yellow needles.  $\alpha$ -Coniceïne solidifies at very low temperatures, and melts at about  $-16^{\circ}$ . Its sp. gr. is 0.893 at  $15^{\circ}$ . It is a tertiary base, and forms a *methiodide*,  $C_8H_{15}N, MeI$ , when treated with methyl iodide. This, when digested with silver chloride, yields the corresponding *chloride*, which forms a *platinochloride*,  $(C_8H_{15}NMe)_2PtCl_6$ . When treated with silver oxide, the iodide yields a strongly alkaline hydroxide. On distilling this hydroxide several volatile bases were obtained, amongst which  $\alpha$ -coniceïne was detected.

$\alpha$ -Coniceïn may also be obtained when conine hydrochloride (1 mol.) is mixed with bromine (1 mol.), and the mixture treated with an alkali, a bromo-derivative,  $C_8H_{16}NBr$ , being formed, in which the bromine has displaced one of the hydrogen-atoms in the imide-group. This compound, when treated with sulphuric acid, yields  $\alpha$ -coniceïne according to the equation  $C_8H_{16}NBr = HBr + C_8H_{15}N$ . When  $\alpha$ -coniceïne is digested at  $200^{\circ}$  with concentrated hydriodic acid and phosphorus, conine is re-formed. If the tempera-

ture is allowed to go much higher than this, or if conine is heated at 300° for some hours with phosphorus and hydriodic acid, an octane and ammonia are formed. The boiling point of this octane is 118—120°, and its sp. gr. 0.712 at 11°. It is impossible to say at present whether this is normal octane or not. It is probable that in the above reaction an intermediate primary amine,  $C_8H_{17}NH_2$ , is formed. By stopping the reaction before its completion, the author was able to detect traces of a primary amine, but did not obtain it in sufficient quantity to determine whether it was the expected compound,  $C_8H_{17}NH_2$ .

The easily soluble and non-crystallisable portion of the picrate prepared from the decomposition-product of conhydrine, yielded  $\beta$ -coniceïne and another liquid base, which the author has not isolated, but which appears to be isomeric with  $\alpha$ - and  $\beta$ -coniceïne. The purification of  $\beta$ -coniceïne is exceedingly difficult, and the author did not succeed in obtaining it absolutely anhydrous.

$\beta$ -Coniceïne is a clear colourless liquid, which at low temperatures crystallises in needles melting at 41°; it does not change when exposed to the air. It boils at 168°, and has the peculiar odour of conine. It forms a stable *hydrochloride*, crystallising in colourless prisms, easily soluble in water. Its *aurochloride* crystallises in well-formed plates, and furnishes the best means of purifying the base. The *platinochloride* forms very soluble crystals.  $\beta$ -Coniceïne may also be obtained by the action of hydriodic acid on conhydrine. In spite of its high boiling point, it is very volatile.  $\beta$ -Coniceïne is a secondary base, and when treated with methyl iodide yields a *dimethylated ammonium iodide*. This iodide was converted into the corresponding *chloride* by digestion with silver chloride. The chloride forms a *platinochloride*,  $(C_8H_{14}NMe_2)_2PtCl_6$ , crystallising in easily soluble prisms and a sparingly soluble *aurochloride*,  $(C_8H_{14}NMe_2)AuCl_4$ .

Prof. Kronecker is now studying the physiological action of  $\alpha$ - and  $\beta$ -coniceïne. He finds that the action of  $\alpha$ -coniceïne is similar to that of conine, but that a much smaller dose is fatal. The action of the  $\beta$ -compound appears to be very much less powerful.

If conhydrine is heated for some hours at 180° with four times its weight of hydriodic acid and a little phosphorus, a crystalline compound,  $C_8H_{16}IN, HI$ , is formed; if the temperature is allowed to rise much higher, the principal product is octane. This compound,  $C_8H_{16}IN, HI$ , which crystallises in sparingly soluble needles, is the *hydriodide* of an *iodoconine*, and is formed according to the equation  $C_8H_{17}NO + 2HI = C_8H_{16}IN, HI + H_2O$ . It gives up all its iodine when boiled with silver nitrate. When treated with silver chloride in the cold, it is converted into the crystalline *hydrochloride* of the *iodo-base*, which yields a *platinochloride*,  $(C_8H_{16}IN)_2, H_2PtCl_6$ . When the iodide is boiled with excess of silver chloride, it yields the *hydrochloride* of a *chloroconine*,  $C_8H_{16}ClN, HCl$ , crystallising in scales. This latter forms a *platinochloride*,  $(C_8H_{16}ClN)_2, H_2PtCl_6$ , crystallising in yellow soluble needles. When the iodoconine hydriodide is treated with reducing agents, such as tin and hydrochloric acid, conine is formed. When the iodide is treated with alkali, the free base,  $C_8H_{16}IN$ , is liberated; this is stable at ordinary temperatures, but if heated

slightly above  $100^{\circ}$  it is converted into coniceïne hydriodide,  $C_8H_{15}N, HI$ . In this reaction, both  $\alpha$ - and  $\beta$ -coniceïne appear to be formed, but sometimes the  $\alpha$ -compound is present almost exclusively, sometimes the  $\beta$ -compound greatly preponderates. The  $\alpha$ -compound preponderates if the iodide is treated with excess of caustic soda and distilled by steam; the  $\beta$ -product if a mixture of the iodide with lime is distilled.

Phosphorus tribromide appears to act on conhydrine in a similar manner to hydriodic acid, and to produce the corresponding bromo-derivative,  $C_8H_{15}BrN, HBr$ .  
L. T. T.

**Paraxanthine.** By G. SALOMON (*Chem. Centr.*, 1884, 490).—The preparation of this compound has been previously described (Abstr., 1883, 601). It is obtained as a loose white scaly mass of silky lustre. Its formula appears to be  $C_7H_8N_4O_2$ , but its properties are distinct from those of theobromine and dioxymethylpurine. Paraxanthine exists as such in urine, and is not produced by the action of the reagents employed.  
A. K. M.

**Alkaloids of Aconitum Lycoctonum.** By DRAGENDORFF and SPOHN (*J. Pharm.* [5], 10, 361—368; from *Pharm. Zeit. Russ.*).—The roots are extracted with alcohol acidified with tartaric acid, the solution evaporated, resins and oils, &c., removed by filtration and shaking with ether; and after making just alkaline with sodium hydrogen carbonate, again extracted, first with ether and secondly with chloroform. From the ether 1.13 per cent., and from the chloroform 0.8 per cent. of alkaloids were obtained.

The first alkaloid, *lycaconitine*, appears to have the composition  $C_{27}H_{34}N_2O_6 + 2H_2O$ ; it is not crystalline, neither is the aurochloride or platinochloride. The authors conclude that it differs from the alkaloids acolyctine and lycoctonine obtained by Hübschmann, and also from aconitine and néphaline. If heated with water under pressure, an acid reaction is developed due to the formation of a volatile acid and a crystalline acid, *lycoctonic acid*,  $C_{17}H_{18}N_2O_7$ ; two alkaloids remain dissolved, one *lycaconine*, soluble in ether, the other soluble in chloroform, and apparently Hübschmann's acolyctine. Lycaconitine, when heated with caustic soda solution under pressure, gives the above-mentioned lycoctonic acid, also lycoctonine and acolyctine; these alkaloids do not occur ready formed in the root, as found by Hübschmann, but are produced by the action of sodium carbonate.

The second alkaloid extracted by chloroform is *myoconitine*,  $C_{27}H_{30}N_2O_6 + 5H_2O$ . It is amorphous. When heated with water or caustic soda, it is decomposed in a manner similar to lycaconitine.

H. B.

**Alkaloids of Coptis Trifolia.** By J. J. SCHULTZ (*J. Pharm.* [3], 14, 273—276).—Coarsely powdered *Coptis trifolia* yields 10 per cent. extractive matter to alcohol (U. S. P.), slightly acidulated with acetic acid. It contains berberine = 0.8 per cent. berberine sulphate and 0.012 per cent. of a second alkaloid. Berberine is only partially extracted from *Coptis trifolia* by the methods usually employed for its determination.  
D. A. L.

**The Alkaloid of *Macleya cordata*.** By J. F. EIJKMAN (*Chem. Centr.*, 1884, 727).—*Macleya cordata* belongs to the Papaveraceæ, and grows wild on the hills and mountains of Japan. The author has extracted from the plant an alkaloid which he names *macleylene*. It is crystalline, tasteless, and melts at  $205^{\circ}$ . The salts are bitter, have an acid after-taste, and produce a sensation of cold. Ultimate analysis and the composition of the platinochloride lead to the formula  $C_{20}H_{19}NO_5$ . Various vivid colorations, described in the paper, are produced by *macleylene* in contact with sulphuric, nitric, and molybdic acids, or certain admixtures of them. R. R.

**The Poisonous Constituents of *Skopolia japonica*.** By J. E. EIJKMAN (*Chem. Centr.*, 1884, 747).—The root of *Skopolia japonica*, one of the Solanaceæ, has been introduced into the European market under the name of "Japanese belladonna." The author has isolated three principles from the root: *skopoletin*,  $C_{12}H_{10}O_5$ , crystallising in slender needles melting at  $198^{\circ}$ , and subliming at higher temperatures: *skopoleine*, a crystalline alkaloid; apparently, it yields atropic acid when digested with baryta-water; *skopolin*,  $C_{24}H_{30}O_{15} + 2H_2O$ , the glucoside of skopoletin. This last substance has not the property of dilating the pupil possessed by skopoletin in a high degree. R. R.

**Formation of Ptomaines in Cholera.** By A. VILLIERS (*Compt. rend.*, 100, 91—93).—The bodies of two patients, sixty-three years of age, who had died from cholera, were examined for alkaloids by Stas's method, twelve and twenty-four hours respectively after death. In both cases an alkaloid was found in notable quantity (at least 0.02 gram of hydrochloride) in the intestines, and in distinct traces in the kidneys; but the liver and the blood in the heart contained a barely appreciable quantity. This alkaloid is a liquid with a sharp taste, and a somewhat distinct odour of hawthorn. It yields a hydrochloride which is neutral to litmus, and crystallises in long, slender, transparent, and highly deliquescent needles. Solutions of the alkaloid give the following reactions: with mercuric potassium iodide, a white precipitate; iodine solution, a brown precipitate, even in solutions which are so dilute that they give no precipitate with mercury potassium iodide; bromine-water, a yellow precipitate; picric acid, a yellow precipitate; gold chloride, a yellowish-white precipitate; tannin or mercuric chloride, a white precipitate in concentrated solutions; platinum chloride, or potassium dichromate, no precipitate; strong sulphuric acid, a pale fugitive violet coloration. With potassium ferricyanide and ferric chloride, the alkaloid does not give the ptomaine reaction immediately, but the reaction develops very slowly.

6 mgrms. of the hydrochloride in 0.5 c.c. of water injected under the skin of the thigh of a guinea-pig, produced very marked periodic variations in the contractions of the heart, followed 45 minutes after injection by violent trembling of the limbs, which rapidly passed away. The animal refused nourishment and died four days afterwards.

The presence of the alkaloid in the kidneys, although only in small quantity, and its almost complete absence from the liver and blood, point to a rapid elimination by the urine. C. H. B.

**Chemical Constitution of Cartilage.**—By C. F. W. KRUKENBERG (*Zeit. f. Biol.*, 20, 307—326).—Friedleben was amongst the first to observe that hyaline cartilage when macerated in dilute acid for several days, yielded a gelatinous solution in which the reactions of so-called chondrin are absent, but those of gluten (gelatin) are observed. Schultze and others attribute this to some unexplained changes occurring during the process of ossification. The author refers to his previous researches on the analogy between the process of ossification and that of new tissue formation, as throwing considerable light on the subject. Bödecker found that on boiling cartilage with mineral acids, a substance was obtained, which he named chondroitie acid. Schiff, however, was the first to see that the change was but a step in the transformation of albumin into carbohydrates; he did not, however, pursue the subject, and it was neglected by other investigators.

The author made four preparations of this so-called chondroitie acid, and subjected them to searching examination with numerous reagents; he concludes that all the end-products of the hyaline series are sugars of different compositions, and that hyaline substances are present, not only in cartilage, but in brain matter, liver, lungs, and in many normal and pathological fluids, and that they are evidences of a process of transformation into pure carbohydrates. J. F.

**Composition of Albuminoids.** By CHICHKOFF (*Bull. Soc. Chim.*, 42, 318).—The author's experiments lead him to the supposition that albuminoids are formed by the reaction of fatty acids with sugar and ammonium nitrate, water being eliminated. When acted on by ferments, albuminoids yield sugar; their transformation into fats under certain pathological conditions indicates a relation to the paraffinoid acids. An acid was isolated from adipocere, which had the properties of stearotic acid. The formation of neurine by the decomposition of certain albuminoids by living cells or micro-organisms, is explained by the action of  $N_2O$  from ammonium nitrate on sugar, thus:—



W. R. D.

**Diffusion of Albumin Solutions.** By E. v. REGECHY (*Bied. Centr.*, 1884, 789).—Albumin diffuses best into a solution of sodium chloride, and the salt solution should be concentrated. Dilute solutions of albumin diffuse best, and they should be pure; pressure aids the diffusion. In a mixture of salts and albumin, the albumin diffuses last, but the diffusion is more rapid when the membrane is thick.

E. W. P.

**Comparative Experiments, with Alkali-albuminate, Acid-albumin, and Albumin.** By A. ROSENBERG (*Chem. Centr.*, 1884, 376—377).—For the preparation of the albuminate, egg-albumin was dialysed for two days so as to remove as much of the salts as possible, and after diluting and filtering through linen, caustic soda was added



(14 c.c. of normal sodium hydroxide to 100 c.c. of the original solution of albumin), and the liquid heated for some hours. On accurately neutralising with hydrochloric acid, the albuminate was precipitated, and after thoroughly washing, was found to be almost free from ash. Neutral solutions of alkali-albuminate obtained by dissolving this albuminate in the smallest possible quantity of soda, become coagulated on the addition of a 10 per cent. solution of sodium chloride, the coagulation being the more rapid the stronger the solution of albuminate, and the larger the quantity of salt added. Thus a 5 per cent. solution of albuminate does not become coagulated until after several days, even when the salt solution added amounts to one-tenth of its volume. Solutions of acid-albumin (prepared either by acidifying the alkali-albuminate with acetic or hydrochloric acid, or by dissolving the albuminate itself in acids) undergo similar coagulation on the addition of neutral salts. On dialysing serum or egg-albumin in their naturally alkaline condition, the power of coagulation first disappears in 48 hours' time, alkali-albuminate being formed on heating; on continuing the dialysis, however, the power of coagulation is restored, owing to the removal of alkali, whilst salts still remain; on continuing the dialysis still further, the power of coagulation again disappears, and on the seventh or eighth day boiling merely produces more or less opalescence. The solution is now neutral and remains so on boiling. If this boiled solution is evaporated to dryness in a vacuum, a residue is obtained, which is perfectly insoluble in water. The same results are obtained by the dialysis of albumin which has been treated with 0.25 per cent. hydrochloric acid. In the undialysed blood-serum of the ox, 9.61—9.82 per cent. of soluble and 1.26—0.81 per cent. of insoluble salts were found, whilst after exhaustive dialysis, only  $\frac{1}{6.8}$  to  $\frac{1}{30.0}$  of the soluble, and  $\frac{1}{14.0}$  to  $\frac{1}{5.8}$  of the insoluble salts were present; the latter consist almost exclusively of ferric phosphate with traces of earthy phosphates.

The opalescence obtained by boiling solutions of albumin, from which the salts have been almost wholly removed, was found to be due to solid particles, the light which such solutions reflect being polarised. This opalescence the author regards as the first indication of coagulation dependent on the presence of the minute proportion of salt, which still remains in the albumin; highly concentrated solutions of this kind become coagulated in 24 hours on the addition of a small quantity of sodium chloride.

P. F. F.

**Solubility of Fibroin.** By LIDOFF (*Bull. Soc. Chim.*, **42**, 318).—Fibroin dissolves in oxalic, gallic, citric, and tartaric acids, as well as in pyrogallol when these are melted, and also in lactic acid when heated with it in sealed tubes. Fibroin can be precipitated by tannin, or by concentrated solutions of neutral salts from dilute aqueous solutions, whilst from its solution in oxalic acid the fibroin is precipitated by 96 per cent. alcohol.

W. R. D.

**Method of obtaining Hæmoglobin Crystals.** By S. v. STEIN (*Chem. Centr.*, 1884, 538).—A drop of blood is placed upon an object-glass and exposed to the air until it begins to dry at the edges;

Canada balsam is then added, first round the blood and then to fill up the space. The layer of blood must not be too thick. Canada balsam which is yellow and not quite clear is best suited for the purpose. The blood must remain for a few days exposed to the air, that is until crystallisation has ceased and the odour of the balsam vanished. The excess of balsam is then removed with the help of a knife, wetted with ether, turpentine, or oil of cloves; the preparation is then covered with a glass, which is fixed on with asphalt or balsam.

A. K. M.

**Study of Metahæmoglobin.** By A. JÄDERHOLM (*Zeit. f. Biol.*, **20**, 419—448).—For the purpose of obtaining metahæmoglobin crystals, the author treated dog's blood, with slight modifications, according to the sixth process described in Preyer's "Die Blutkrystalle." The crystals differ only in size and shape from those Hammarsten obtained by treating horse's blood with ferricyanide of potassium and subsequent dilution and application of cold (*Zeit. Physiol. Chem.*, **8**, 186), as both forms of crystals and their solutions give the characteristic spectra of metahæmoglobin.

The addition of a very small quantity of sodium carbonate (0.00053 per cent.) to a solution, produces the so-called alkaline metahæmoglobin spectrum  $\pi + \alpha_1 + \beta_1$ ,  $\pi$  being always weaker than  $\alpha_1 + \beta_1$ .

The bands II and III of metahæmoglobin, and  $\alpha_1 + \beta_1$ , of its alkaline solution, correspond very nearly with  $\alpha + \beta$  of oxyhæmoglobin. The spectrum  $\pi + \alpha_1 + \beta_1$  of alkaline metahæmoglobin can be obtained also by passing pure hydrogen through a solution.

If excess of sodium carbonate be avoided on the one hand, and of hydrogen on the other, the bands I and IV of metahæmoglobin are produced on shaking the solutions with air.

The latter half of the paper is devoted to the discussion of its constitution. The author explains his reason for assuming it to be a peroxidised oxyhæmoglobin, as he did in his former paper, but now agrees with Hüfner and Hülz in considering it to contain the same amount of oxygen as oxyhæmoglobin.

J. P. L.

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## Physiological Chemistry.

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**Influence of Variations in the Percentage Composition of the Air on the Intensity of Respiratory Changes.** By L. FRÉDÉRICQ (*Compt. rend.*, **99**, 1124—1125).—The author has investigated the influence of variations in the amount of carbonic anhydride or of oxygen in the air on the intensity of respiratory changes, as measured by the amount of oxygen absorbed in the case of rabbits and of himself.

An increase in the proportion of oxygen has no effect on the absorption of oxygen in the process of respiration. When an animal is

transferred from ordinary air to an atmosphere of oxygen, or one containing a high proportion of oxygen, there is at first an increase in the amount of oxygen absorbed, owing to the dissolution of this gas in the plasma of the blood and lymph, but as soon as equilibrium is established between the tension of the oxygen in the plasma, and that of the atmosphere in the lungs, the absorption of oxygen returns to its normal amount. This result was previously arrived at by Speck. The respiration of an atmosphere poor in oxygen produces, as is well known, more or less intense dyspnœa.

Man can breathe for a long time an atmosphere which is rich in oxygen, but contains from 5 to 6 per cent. or even more carbonic anhydride. Under these conditions a peculiar kind of dyspnœa is produced, characterised by troubled, more or less convulsive, respiration, and a cephalalgia resembling headache. This dyspnœa is quite distinct from that caused by a deficit of oxygen, and is accompanied by a notable increase in the amount of oxygen absorbed. It follows that carbonic anhydride in small quantities acts as a powerful exciter of respiratory combustion.

Previous experimenters have found that carbonic anhydride diminishes the amount of oxygen absorbed, but they used large proportions of the gas, and their results are vitiated by the direct poisonous action of the anhydride. C. H. B.

**Differences between Pepsin and Trypsin.** By E. BOURQUELOT (*J. Pharm.* [5], 10, 177—187).—Pepsin is said to exercise its digestive action only in acid solution, whilst trypsin acts only in alkaline, neutral, or feebly acid solutions. But though the first statement is true, the second requires modification, since 0.10 per cent. of acetic or 0.03 per cent. of hydrochloric acid may be present, without stopping the digestion, and the gastric juice generally contains only 0.02 per cent. The characteristic swelling which takes place when fibrin is acted on by the gastric juice, is moreover not due to the pepsin contained, but to the acid. The difference in the action of gastric juice and pancreatic juice on milk is also due to the acidity of the former. The products of the gastric and pancreatic digestion of fibrin do not differ except in the first products, which are respectively a syntonin and a globulin, and this difference loses its significance since syntonin is produced, though somewhat slowly, by the action of hydrochloric acid alone. The difference in the action of the products of the two digestions on polarised light also is due, not to any difference in the peptones produced, but rather to the action proceeding further in one case than in the other.

Kühne found that trypsin is destroyed by gastric juice; if a similar action is exerted on other ferments, such as that of the saliva or diastase, this action may be utilised to detect pepsin. But here again the amount of acid present and necessary for the action of the pepsin, must be considered. The ferment of the saliva and the diastase of malt are not destroyed by treatment with hydrochloric acid of 0.01—0.50 per cent. for five hours at 18°; but the action of saliva on starch-paste is stopped by the addition of an amount of acid sufficient to destroy the original alkaline reaction, and hence the digested liquid

must first be exactly neutralised before testing its action on starch. Knowing these conditions, it is thus possible to determine whether a liquid, digesting proteids, contains pepsin or trypsin. H. B.

**Metabolism of Five Children of Ages varying from 5 to 15 Years.** By W. CAMERER (*Zeit. f. Biol.*, 20, 566—583).

**Influence of Meat Extract on the Temperature of the Body.** By M. RUBNER (*Zeit. f. Biol.*, 20, 265—276).—The author, from the result of previous experiments, believed that the extractive matter of meat had no part in the production of bodily heat, but passed away, without important change, in the urine; the experiments of Kemmerich are referred to, in which he failed to keep animals alive on a diet of meat extract, and the fact is noted that after a meal of meat extract there is more carbon found in the urine than should be present normally. In order to study the question, the author made an experiment with a dog weighing 24 kilos., and which generally consumed daily 2 lbs. of flesh. The animal was left unfed for two days; on each of the two following days 500 c.c. of solution of meat extract, equal to 2 lbs. flesh, was given; the following day he received no food. The day before the experiment he drank 200 c.c. of water, but none in the course of the experiment. The animal took the solution readily and lay quietly in the experimental chamber, in which daily estimations of respiratory products were conducted. The voided urine was of a fine golden-yellow, darker than the urine passed after a diet of washed flesh. On evaporation, when the bulk of the water had been removed, the peculiar smell of extract of meat was clearly perceptible; this was not the case during feeding with meat or on the hunger days. The carbonic anhydride expired in the two days of hunger amounted to an average of 264.24 grams for 24 hours, and on the two days when meat extract was supplied to 263.84 grams for 24 hours; so that the carbon of the extract did not pass in the respiration, and the body substance was plainly unchanged.

Examination of the urine showed some interesting facts. During the hunger days at the commencement of the experiment, the nitrogen passed was 4.75 grams in 24 hours; the two days of extract feeding showed 6.96 and 6.67 grams respectively; it fell to 4.08 grams when the food was withheld. Phosphoric acid varied more irregularly.

The author gives details of the processes used in the various experiments, but comes to the general conclusion that it is impossible that the meat extract experiences any change in its passage through the system, and that it does not in the least contribute to bodily heat; the waste of tissue is neither hastened nor retarded by it, and it passes away unaltered in its composition. J. F.

**Influence of Certain Amides on the Animal Organism.** By H. WEISKE and B. SCHULZE (*Zeit. f. Biol.*, 20, 276—285).—A series of experiments on various herbivorous mammalia and geese convinced the authors that the considerable quantity of asparagine frequently present in fodder is not unimportant, but can replace a part of the albumin, without the production of milk or the growth of

flesh suffering any diminution. Zuntz (Abstr., 1884, 472) reports the results of his experiments on rabbits, whereby this property of asparagine is confirmed; whilst it is shown that other amides, tyrosine, taurine, &c., have quite a contrary effect and cause considerable waste of albumin. Potthast (*Pflüger's Archiv*, 32, 280) also believes that the combustion of asparagine in the body diminishes the waste of tissue and acts as a true food. Schrodtt, in his report of the experimental dairy farm at Kiel (Abstr., 1884, 1396), found that the milk did not suffer either in quality or quantity, when a part of the usual fodder was replaced by malt combings which contain much of their nitrogen in the form of asparagine.

These experiments were made on the herbivora, because it has been shown by Munck (*Virchow's Archiv.*, 94, 426) that asparagine, when added to the food of carnivora (a dog), acted as a diuretic, and caused increased production of both nitrogen and sulphur compounds. Knieriem, however, has made experiments on a dog, with different results. The authors wished to determine whether this property is peculiar to the asparagine itself, or if it possesses it in common with other related compounds. The substances taken for experiment were amidosuccinic acid and succinamide, the subject of experiment being a large gander. A larger animal, such as a sheep, would have required too much of the costly substances used, besides which, the collection of the excrement for analysis was easier. Full details are given of the food, its preparation and composition, and the mode of analysis adopted for the excrement. The weight, &c., of the animal was taken daily. It was found that the addition of the two substances to the food caused very little difference in the quantity of nitrogen excreted, the succinamide slightly increasing the amount, but not to an important extent. Tables accompany the paper. J. F.

**Digestibility of Lucerne and Clover Hay by the Horse and Sheep.** By E. WOLFF and others (*Bied. Centr.*, 1884, 751—752).—The horse was 8—9 years old, the two sheep were 1½ years old; and they were fed with lucerne cut on May 30th, and made in eight days. A second cutting (not aftermath) was made three weeks afterwards, and is designated as lucerne 2; the clover hay was made when the bloom was out. The horse had gentle exercise every day, and its weight consequently remained unaltered. The coefficients of digestion are as follows:—

		Dry matter.	Organic matter.	Albu- min.	Fat.	Fibre.	Extrac- tive.
Lucerne 1	{ horse ....	60·78	61·47	74·78	29·81	43·96	71·26
	{ sheep ....	59·28	60·93	71·23	56·25	46·08	67·98
Lucerne 2	{ horse ....	55·54	55·22	70·36	21·11	36·32	67·24
	{ sheep ....	56·33	57·94	68·22	49·16	46·83	63·72
Red clover	{ horse ....	54·52	54·68	60·02	30·74	38·60	66·56
	{ sheep ....	53·90	55·34	54·51	57·61	47·78	61·20

All previous experiments have shown that meadow hay is better digested by the sheep than by the horse; these experiments, however, show but little difference save in the fat and fibre. It is evident from the above table that a horse can be kept in fair working condition on lucerne hay alone, but such is not the case with meadow or clover hay. E. W. P.

**Digestibility of Clover and Meadow Hay by the Horse and Sheep, and the Elimination of Mineral Matter by the Horse.** (1882.) By E. WOLFF and others (*Bied. Centr.*, 1884, 753—755).—In this series, two sheep were compared with one horse as regards their power of digesting clover and meadow hay, and the coefficients are as follows:—

		Organic matter.	Albu-min.	Fat.	Fibre.	Extrac-tive.
Meadow hay ..	{ sheep .....	63·00	58·80	51·79	62·11	65·39
	{ horse .....	50·02	55·07	9·81	40·50	58·23
Red clover hay	{ sheep .....	57·64	56·84	62·35	49·94	64·30
	{ horse .....	52·50	57·02	28·20	39·02	64·36

Again, the difference in the digestion of fat and fibre is remarkable. Examination of the excreta of two horses was made, and the following table shows the percentage of the ash constituents in the hay excreted.

	Ash.	K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	Cl.
Meadow hay—								
horse 1 ..	63·8	36·6	63·0	31·7	76·7	116·7	30·7	12·7
„ 2 ..	61·4	29·2	46·1	34·5	68·0	116·1	52·2	9·4
Clover—								
horse 1 ..	57·2	30·0	100·0	37·3	87·5	102·4	26·1	16·8
„ 2 ..	53·1	28·9	100·0	45·7	47·4	100·7	37·3	10·5

E. W. P.

**Sugar in Blood: its Source and Signification.** By J. SEEGEN (*Bied. Centr.*, 1884, 747).—Earlier investigations by the author showed that the formation of sugar was a physiological function of the liver, and that it was independent of the food. Later investigations on dogs show that sugar is always present in blood to the extent of 0·1—0·15 per cent., and that the quantity in cardiac and arterial blood is the same; there is, however, a variation, within small limits, in the percentages existing in arterial and venous blood, whilst mesenteric blood always contains less sugar than blood from the carotid.

The blood issuing from the liver contains twice as much sugar as that entering, the quantities being 0·230 per cent. and 0·119 per cent. Passing to absolute quantities, there was produced during

24 hours, by the livers of three dogs weighing 7, 10, and 11 kilos., 179, 233, and 433 grams sugar respectively. As far as can be ascertained, the albumin is the source of sugar in carnivora, and as the sugar is not eliminated as such, it follows that its decomposition must be accomplished in the circulation.

E. W. P.

### Influence of Asparagine on the Elimination of Albumin.

By J. MUNK and C. v. VOIT (*Bied Centr.*, 1884, 749—750).—Weiske and others consider that asparagine aids in preventing the loss of albumin from the animal system, but these two authors independently, and by different methods of experiment, come to the same conclusion, namely, that asparagine does not prevent the decomposition of albumin in the organism, but rather assists it; and its after-action on the elimination of water and decomposition of albumin leave no doubt that it cannot be considered to be a food, at least, for the carnivora.

E. W. P.

### Influence of Bodily Labour on the Discharge of Nitrogen.

By W. NORTH (*Proc. Roy. Soc.*, 36, 11—17).—Parkes found that bodily exercise caused a slight increase in the discharge of nitrogen during and immediately after labour, although his experiments leave the question undecided whether this increase occurs at the expense of stored material independently of any concomitant or subsequent increase of intake. In order to decide this problem, the author carried on a series of investigations on himself for certain intervals of time, during which a regulated diet of accurately known composition was taken. During the interval, a known amount of muscular labour was performed. In order to get rid of any possible surplus of nitrogen in the body, either the diet was regulated for four or five days before beginning an experiment, or, better, food was abstained from on the first day of an experiment. The table below illustrates the results obtained in one of the series of experiments:—

Daily.	Before work.	After work.	Difference.
Nitrogen of urine . . . .	14.15 grams	15.74	1.59
"      faeces . . . .	2.48 "	2.15	0.33
P <sub>2</sub> O <sub>5</sub> of urine . . . . .	2.01 "	2.00	0.01
P <sub>2</sub> O <sub>5</sub> of faeces . . . . .	2.54 "	1.85	0.69
H <sub>2</sub> SO <sub>4</sub> in urine . . . . .	2.76 "	3.00	0.24

The work done was a walk of 30 miles at the rate of 4.28 miles per hour, a load of about 27 lbs being carried.

The general results, while confirming those of Parkes, show that the disturbance produced by severe labour is more immediate and of greater intensity than hitherto supposed. Further, that a diminution of the nitrogen stored in the system is followed by a retention, that is, by a condition in which the intake is greater than the output. Thus the storage of nitrogen represents the tendency of the organism to economise its resources. Finally, unless the exertion be very severe, the elimination of phosphates is not altered, while the output of sulphates is markedly increased.

V. H. V.



**Iodine in Human Urine after the External Application of Iodoform.** By J. GRÜNDLER (*Chem. Centr.*, 1884, 492).—In a few cases of the application of iodoform, no iodine was found in the urine, but in all other cases in which poisoning did not occur, the iodine is present in the urine chiefly as potassium iodide, but to some extent also as iodate. In cases of poisoning by iodoform, the iodine is discharged not so much in the form of potassium iodide, as in combination with organic compounds. From this it is concluded that if a means were discovered by which the iodine could be converted, before its absorption, into potassium iodide, a protection against poisoning might be secured.  
A. K. M.

**Occurrence of Hydroxybutyric Acid in the Urine in Cases of Diabetes Mellitus.** By O. MINKOWSKI (*Chem. Centr.*, 1884, 406—407).—The author has proved the presence of this acid in a case of diabetes mellitus, accompanied by increased excretion of ammonia.  
P. F. F.

**Hydroxybutyric Acid in Diabetic Urine.** By O. MINKOWSKI (*Chem. Centr.*, 1884, 672).—Hydroxybutyric acid obtained from urine is in many respects remarkably similar to Wislicenus'  $\beta$ -hydroxybutyric acid, but the two are not identical, as the latter is optically inactive.  
R. R.

**Nitrates in Urine.** By T. WEYL (*Bied. Centr.*, 1884, 856).—When normal human urine is distilled with addition of sulphuric and hydrochloric acids the distillate frequently gives the characteristic reactions of nitric acid, and from it is obtained by oxidation a body which, when heated with ferrous chloride and hydrochloric acid, evolves nitric oxide; nitrates must therefore be assumed to be present until it is shown that other substances giving similar reactions occur in the urine.

The author's experiments show that under favourable conditions, nitrous acid can exist for a short time in presence of urea.  
J. F.

**Phenaceturic Acid in the Urine of Horses.** By E. SALKOWSKI (*Ber.*, 17, 3010—3012).—The urine of the horse contains about 0.5 of a gram of phenaceturic acid per litre. When the hippuric acid is precipitated by hydrochloric acid, the phenaceturic acid remains in the solution, from which it may be extracted by ether.  
W. C. W.

**Chemical Composition of Pig's Urine.** By G. SALOMON (*Chem. Centr.*, 1884, 347—348).—The urine of the pig presents some points of similarity to that of man, which is not surprising considering the omnivorous habits of both. Uric acid, however, which is such an essential constituent of human urine, had not previously to the author's observations been found in the urine of the pig. By employing the process of precipitation with silver nitrate, as described by Salkowski and Leube (*Lehre vom Harn*, § 96), the author obtained 0.65 gram uric acid from  $5\frac{1}{2}$  litres of pig's urine. This quantity, although considerably less than that present in human urine, is in excess of what is found in the case of other families, such as the

carnivora and herbivora. One determination showed the proportion of uric acid to urea to be as 1 : 150. The author also finds two substances belonging to the xanthine-group, of which one appears to be guanine, and the other xanthine itself; creatine and an acid soluble in ether were also found. P. F. F.

**Physiology of Uric Acid.** By A. B. GARROD (*Proc. Roy. Soc.*, 37, 148—150).

**Nitrogen in Fæces.** By H. RIEDER (*Zeit. f. Biol.*, 20, 378—395). —The estimation of nitrogen in the fæces of animals is of great importance in physiological investigations, particularly in those connected with the digestion of food, but as there are always present residues of the digestive fluids, mucus, epithelium of the intestines, &c., it is desirable that a correct idea of the probable amount of such matters should be obtained, in order to make allowance for them in investigations. It is probable that the black pitchy matter passed in small quantities by animals after long fasting, is a fair guide to the amount. In Voit's laboratory, several dogs were left hungry for long periods, and it was found that for dogs averaging 26 kilos. the quantity of dry excrement averaged 3·2 grams per day; this, compared with the animals after plentiful feeding on flesh, is remarkable, as during that time only 11 grams of dry matter were passed; the amount passed during hunger, therefore equalled 36 per cent. of the total. The author reviews the experiments which have been made by other investigators, and describes some of his own. A small dog, weighing 7 kilos., kept fasting for nine days, passed during that time 11·88 grams fæces containing 7·12 per cent. nitrogen, or daily 1·32 grams fæces with 0·094 gram nitrogen. When fed for a time on 70 grams of air-dried starch-flour and 6·4 grams fat, and on a second occasion on 140 grams daily of the same food, with addition of 11·3 grams of fat; the results showed that on a diet free from nitrogen, the fæces contain more nitrogen than during the hunger period, and as much as during a flesh feeding period. The activity of the processes in the intestine causes greater secretion and excretion. When dogs are fed on bread or potatoes, the case is different, the amount of excrement is greater, but consists largely of undigested or little altered matter.

The question is of great importance as regards human beings; besides quoting the experiments of Rubner and of Parkes, the author gives details of some of his own. A man weighing 70 kilos. received daily about 600 grams of dry substance consisting of 300 grams of starch-flour (86·24 per cent. dry substance), 120 grams sugar, 89 grams suet, 12 grams cream of tartar, and 5 grams sodium bicarbonate; for drink, on the average, he received 908 c.c. light white wine in mineral or carbonated water daily; the experiment lasted three days. The same man was the subject of another three days' experiment on less food, namely, for each day, 90 grams starch-flour, 40 grams sugar, 30 grams suet, and 11 grams baking powder, together 158·6 grams dry matter; 1125 c.c. white wine was drunk.

In a third experiment, another man was the subject; he weighed

74 kilos., and received as food 100 grams air-dried starch-flour, 30 grams sugar, 30 grams suet, and 5 grams baking powder; in all containing 147·2 grams dry substance; he drank 907 c.c. of white wine daily. The principal average daily results of these three experiments are thus summarised :—

No. of experimental series.	N in urine. grams.	Fæces.		
		Dry subs.	Per cent. N.	Gram N.
1 .....	9·30	13·4	4·08	0·54
2 .....	9·50	15·4	5·69	0·87
3 .....	7·6	13·4	5·85	0·78

The total nitrogen excreted in the fæces amounts therefore to only about 8 per cent. of the total passed during a non-nitrogenous diet. Rubner's experiments show that an egg or flesh diet does not materially increase the amount; the author is therefore of opinion that the greater part is derived from waste of the walls of the intestine. The author continues his researches, as the subject requires further investigation. J. F.

**Physiological Action of some Ammonium-bases.** By A. GLAUSE and B. LUCHSINGER (*Chem. Centr.*, 1884, 444).—The authors have investigated the action of a number of these trimethylammonium bases, including neurine, muscarine, amyl-, valeryl-, benzyl-, and glyceryl-trimethylammonium, and also tetramethylammonium salts. The general tendency of this class of substances is to depress or even paralyse the action of the heart. P. F. F.

**Anæsthetic Action of Cocaine Hydrochloride.** By J. GRASSET (*Compt. rend.*, 99, 1122—1123).—The injection of 0·01 gram of cocaine hydrochloride beneath the skin of a man produces a very distinct zone of cutaneous anæsthesia, without any general phenomena and without any important after-effects. The anæsthesia lasts sufficiently long for certain surgical operations. At least 0·01—0·02 gram of the hydrochloride should be injected just below the region to be operated on, and the operation should begin 5 or 10 minutes after injection. C. H. B.

**Hygienic Importance of Carbonic Oxide, and its Detection.** By A. P. FOKKER (*Chem. Centr.*, 1884, 380—381).—The author describes a modification of Fodor's method of detecting carbonic oxide. 1—2 c.c. of the blood to be tested for carbonic oxide is placed in a shallow beaker, which is floated in a porcelain dish full of water, the beaker being kept in a vertical position by means of three perpendicular brass wires which carry above a watch-glass containing a little palladium chloride solution. A glass shade is inverted over the beaker so that it stands in the dish of water, and two-thirds of

the air in the glass shade are exhausted by means of an india-rubber tube. The water in the dish is then boiled, which causes the coagulation of the blood in the beaker floating upon the surface of the water, and the carbonic oxide escapes and reduces the palladium chloride in the watch-glass above. If traces only are present, the reduction does not take place immediately, and the apparatus should be allowed to stand for 24 hours. In this manner it is possible to detect the presence of carbonic oxide in a single drop of blood. P. F. F.

**Poisoning by Nicotine.** By RABOT (*J. Pharm.* [5], **10**, 189—193).—Cases of poisoning of nicotine are very rare; in the present case the liquid used for destroying insects on plants was taken in quantity. From the liquid in the stomach, 2.25 grams nicotine were obtained, and traces were found in the bile and urine; ordinary methods of separation were used. H. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Changes which Milk undergoes through the Agency of Micro-organisms.** By F. HUEPPE (*Chem. Centr.*, 1884, 315—316).

—The author points out the chemical changes taking place in the sterilisation of milk by heat. On heating milk above 75°, the action of rennet is retarded, but this retardation can be to a certain extent counteracted by increasing the amount of rennet. Exposure to a high temperature increases the dissimilarity between cow's milk and human milk, and also renders it less digestible, as owing to the impaired action of the rennet the curdling of boiled milk in the stomach is almost exclusively performed by the gastric acids. The digestibility of milk is, however, not materially diminished by temperatures below 100°, and it is, therefore, desirable that in preserving milk the sterilisation should be effected at a temperature not exceeding 100°. This can be done by heating the milk for one hour on five consecutive days at 65°—75°. Milk sterilised in this manner is hardly distinguishable by its taste from fresh milk, but on standing the casein is gradually deposited, so that the supernatant liquid has the appearance of watered milk. The sterilisation can be effected much more rapidly by a current of steam. On inoculating this sterilised milk with a pure cultivation of the lactic ferment, the lactic fermentation was in all cases set up. The activity of these organisms ceases below 10° and above 44·8°—45·5°; they produce lactic acid from milk-sugar, cane-sugar, mannite, and dextrose, and it is probable, therefore, that they do not convert milk-sugar into lactic acid and carbonic anhydride, but that their action consists in the first instance in the hydration of the di-saccharates. The lactic acid bacteria exhibit diastatic action, but no peptonising properties.

The author has also studied the butyric acid bacilli, which he finds in

the first instance curdle the milk like rennet, and, if the initial reaction be neutral or weakly acid, actually dissolve the curd by converting it into peptones and other products of decomposition, amongst which is ammonia, although the bacilli are unable to induce the ammoniacal fermentation of carbamide. The spores of these bacilli are far more refractory than the lactic acid bacilli, thus offering considerable difficulty to the preservation of milk.

The author then treats of the *organisms of blue milk*: these bacteria multiply by fission and by means of spores, they neither curdle nor acidify milk, but on the contrary render it gradually alkaline. The colouring matter which is produced at the expense of the casein, is, in the absence of acid, not sky-blue but rather slate-grey, but becomes intensely blue on the addition of acid. These bacilli, by their action on ammonium tartrate, produce a green colouring matter which is converted into the above blue one by oxidation. There can be no doubt that these bacilli are not only the invariable concomitants of blue milk, but also the inducing cause of this phenomenon. *Oidium lactis* is a fungus which forms a thick white mycelium on the surface of milk, the latter remaining liquid and becoming faintly alkaline. This organism has become erroneously regarded by some as a lactic acid ferment; it only, however, indirectly furthers the production of lactic acid by removing the free acid as it is formed, and thus enabling the lactic organisms to convert fresh quantities of sugar.

P. F. F.

**Origin of Microzymæ and Vibrioles in Air, Water, Soil, &c.** By A. BÉCHAMP (*Compt. rend.*, 100, 181).—A claim for priority.

**Degeneration of Brewer's Yeast.** By H. BUNGENER (*Bull. Soc. Chim.*, 42, 567—573).—As is well known, yeast which has been repeatedly employed for fermenting purposes, becomes after several generations unfit for further use. Numerous attempts to explain this fact have been made, but so far without success. The presence and growth of lactic and acetic ferments along with the *Saccharomyces cerevisiæ* are not sufficient to cause degeneration, as their numbers can be kept down at a minimum in all well-conducted breweries. Doubtless the composition of the wort, the quantities of sugar, extract, and salts, it contains, have a great deal to do with this result, and this is particularly the case with the nitrogenous constituents. Of the latter, certain of the amido-compounds which yield the nitrogen food to the ferment, are the most important. Recent observations have shown that after each fermentation the quantity of nitrogen in the yeast increases, as does also the fermenting power; but after a time the fermentation finishes, leaving the cells still suspended in the liquid, and the yeast is no longer fit to use.

J. K. C.

**Vitality of Germs of Microbes.** By E. DUCLAUX (*Compt. rend.*, 100, 119, and 184—186).—The germs of different species of *Tyrophthrix*, more particularly *Tyrophthrix scaber*, are not killed by at least three years' exposure in a dry state to air at a tropical temperature, but are killed by exposure to sunlight at the same temperature for

some weeks. The exact time required depends on the species and on the nature of the fluid in which it has been cultivated.

The author has also examined various cultivations which have been kept in flasks at the ordinary temperature for several years, including those which were used by Pasteur in 1859 and 1860, and which are consequently 25 years old. The vitality of the germs contained in these flasks was determined by seeding various liquids with the contents of the flasks. Of 27 flasks which originally contained a slightly acid aqueous solution of yeast without sugar, only two contained living germs; of 25 others, 18 contained myceliums which had not fructified. Fifteen flasks of aqueous yeast and sugar contained only three living species, and 10 flasks of milk contained only two living species. In all the flasks which contained living germs, the liquid was *slightly* alkaline, whilst in all the others it was acid. Eight flasks containing aqueous yeast and calcium carbonate all contained living germs. Five flasks containing urine 20 years old, and strongly alkaline, contained no living germs. It would seem, therefore, that *slight* alkalinity is much more favourable than acidity to the preservation of microbes.

Of the 65 flasks examined, 15, or nearly a quarter, contained living germs. Among these were certain known species, such as *Sterigmatocystis migræ*, which, if dried in the air, are dead after the expiration of three years. The liquids also contained several species of *Tyrophthrix*, still in a very active condition, and several new species of microbes.

C. H. B.

**Source of the Nitrogen of the Leguminosæ.** By B. E. DIETZELL (*Ann. Agronomiques*, 10, 543—544).—The author accepts the conclusion of Boussingault, confirmed by Lawes, Gilbert, and Pugh, that plants do not directly assimilate the free nitrogen of the atmosphere. But it still seemed to him possible that leguminous plants should assimilate combined nitrogen directly from the air. In order to test this point under conditions as nearly natural as possible, he has grown clover and peas in pots of ordinary garden soil, in free air, but sheltered from the weather and watered with pure distilled water. A weighed quantity of soil was used in each case, and the nitrogen in it determined (0.415 per cent.). The nitrogen contained in the seeds sown and in the matured plants was also determined. Each series consisted of six pots, No. 1 being without added manure, No. 2 with kainite, No. 3 with kainite and superphosphate, No. 4 with kainite, superphosphate, and calcium carbonate, No. 5 without plants, but with kainite, superphosphate, and calcium carbonate, and No. 6 without plants and without added manure. The results show that peas and clover do not absorb combined nitrogen from the air. In all cases except two there was a *loss*, varying from 5.10 to 15.32 per cent. of the nitrogen in the soil. The two exceptions were, No. 6, the soil without plants and without manure, which gained 0.26 gram nitrogen, and No. 3, peas grown with potash and phosphoric acid, in which there was neither gain nor loss. The author suggests that acid calcium phosphate or bibasic calcium phosphate may react upon the ammonium nitrite formed in the soil, and by converting it into calcium nitrite and ammonium phosphate may prevent its decomposition. J. M. H. M.

**A New Germinator.** By J. KÖNIG (*Bied. Centr.*, 1884, 789).—A zinc trough, 20 cm. broad by 23 long and 4 cm. high is employed, this is divided along the length by a strip of zinc reaching to the bottom, and on each division thus formed is laid a glass sheet 4 cm. broad. Strips of filter-paper,  $9\frac{1}{2} \times 17$  cm., are laid on the glass, so that the ends fall over the sides of the glass into water in the bottom of the trough; the seeds will germinate on this moist paper.

E. W. P.

**Influence of Light on the Germination of Seeds.** By A. CIESLAR (*Bied. Centr.*, 1884, 860).—The author finds that many seeds hitherto thought to germinate in light only, will do so equally well in darkness. Small seeds with poor reserve of material germinate better in light, whilst those with a large reserve do so equally well in darkness; he did not find any seeds which grew better in darkness than in light. Yellow light accelerated, violet retarded germination, and the latter at a low temperature almost rendered growth impossible. In white light, there was greater energy of growth, a higher percentage of buds and generally more activity than with coloured lights; the author thinks this due in part to the transformation of light into heat.

J. F.

**Action of Long Days on Vegetation.** By SCHÜBELER (*Bied. Centr.*, 1884, 791).—By reason of the long days in northern latitudes, plants produce larger and heavier seeds than in the more southerly latitudes; yet although the grain is heavier, the extra weight is not due to nitrogenous matter, which remains unaltered. Leafy plants, such as vegetables, produce larger leaves, and blossoms which are white elsewhere are frequently violet here.

E. W. P.

**Influence of Intermittent Heat on the Germination of Seeds.** By A. v. LIEBENBERG (*Bied. Centr.*, 1884, 756—757).—*Poa pratensis* germinated to the amount of 80 per cent. when exposed to daylight; but when the pots in which the seed was sown, were placed in darkness at 22°, only 2·5 per cent. germinated; from these results, it appeared evident that intermittent light was more effective than high temperature and darkness; to prove this, seeds were placed in front of a window; in the dark at 20°; in the dark at 28°; and a fourth set were alternately in the dark at 20°, and then for 5 hours at 28°. The best results were obtained in this last case, when 23 per cent. germinated, whilst in the second only 1·5 per cent. did so. Several other seeds were tried, and all proved that variable temperatures, even in the dark, were better than exposure to sunlight only.

E. W. P.

**Effects of Running Water on Plants.** By B. JÓNSSON (*Bied. Centr.*, 1884, 860).—When a plasmodium of Myxomycetes in a healthy state is placed on filter-paper, so arranged that a portion of the paper is in contact with water, a movement in the direction of the water is perceived; the author's experiments were made to discover whether the protoplasm of other plants was similarly affected; he found that the hyphen of the spores of mycelia were affected, but that the movements were in the same direction as the flow of water. He placed young plants of maize in such a way that the roots dipped



into swiftly running water; although at first perpendicular, after 20 hours they formed a right angle, their points growing against the stream, and when their position was reversed with the points down stream, they bent until they again brought their points against it.

J. F.

**Water Culture of Lupines.** By TROSCHKE (*Bied. Centr.*, 1884, 850—852).—Lupines have not yet been successfully cultivated in water; the author has been more successful than other experimenters, but still cannot produce plants as healthy as those grown in open soils. The roots of the water-grown plants do not contain those excrescences which are usually present on the roots in a state of nature. These excrescences are connected with a minute fungus, but the manner of their growth is unknown. The author submitted a quantity of them to chemical examination, and found them quite different in composition from the roots proper, being very rich in fat, albumin, and phosphoric acid; the large proportion of nitrogenous matter is similar to that in earth-nut cake, one of the richest feeding materials.

J. F.

**Water Culture of Lupines.** By WEISKE (*Bied. Centr.*, 1884, 790).—Lupine seeds were grown in glass vessels which were more or less tightly closed, other seeds were grown on paper in basins; the solutions contained some nitrogenous, others no nitrogenous plant food constituents. When the plants were dead, they were dried and the nitrogen estimated. It was found that those plants grown in non-nitrogenous liquids contained but very little nitrogen, and that those grown in the basins were the richest in this constituent.

E. W. P.

**Chemical Phenomena of the Respiration of Plants.** By T. L. PHIPSON (*Chem. News*, 50, 288).—In connection with the general idea that the exposure of the green parts of plants to light is sufficient to cause them to breathe, the author remarks that temperature is quite as important an agent. For example: plants were exposed to light on two days of nearly equal photometric intensity of daylight; but when the temperature was respectively 38° F. and 70° F., in the first case the evolution of gas was *nil*, whilst in the second it was abundant. On another occasion a plant at 45° F. in bright sunlight gave no gas, whereas, after an hour at 59° F. in much less powerful light, gas was evolved. The plants employed in these observations are unicellular algæ; they have no stomata, it is therefore inferred that these organs are not indispensable for the respiration of plants. A temperature of from 60° F. to 90° F. and exposure to sunlight appear to be the most favourable conditions for the respiration of these plants. Other observations and experiments tend to show that circulation is closely connected with respiration, and, like it, is equally dependent on temperature as well as light. It is stated that the oxygen evolved from the organisms in stagnant water comes from zoospores, and not from infusoria, as is sometimes supposed. It is inferred that the respiration of plants is independent of chlorophyll, but that chlorophyll is formed by the process of respiration, inasmuch as the brown or yellowish *Protococcus pluvialis* emits oxygen, and algæ accidentally

bleached by adding a minute quantity of sodium hydroxide to the water in which they were being cultivated, after washing and again exposing to light, gave off oxygen after four hours, and the next day developed green patches. The author's experiments negative the idea that for the cultivation of plants, carbonic anhydride may be replaced by organic acids.

D. A. L.

**Evaporative Surfaces of Plants and Influence of Moisture in Soils on Plant Growth.** By H. HELLRIEGEL (*Bied. Centr.*, 1884, 834—849).—The author's previous experiments have convinced him that plants so dissimilar as beans and barley have nearly the same extent of evaporative surface, the measurement of which, although difficult, should afford much information as to the effect of moisture in the soil. These effects have been frequently remarked. The author made experiments with barley grown in soils containing 10, 20, 40, and 60 per cent. of water; with the higher percentages, the size of leaf increased proportionally, but when examined under the microscope the leaves of the plants grown with the lesser quantities of moisture showed far larger numbers of stomata than the others, and in the former the stomata were larger, and the cells more developed. The greater quantity of matter produced by well watered plants, appears to be due to the quick multiplication and development of the cells; in the less watered plants, the contents of the cells appear to be more concentrated.

Plants do not possess the power of assimilating the moisture existing as vapour in the air; the rainfall is therefore a most important factor in the growth of plants in dry soils; the transpiration from the leaves and the loss of moisture from the soil by evaporation serves to balance the effect of excessive rainfall. The author has observed the fall for 15 years at one station, but the conclusions drawn are incomplete. Soils possess this power of absorption of moisture from damp air; the author's experiments show that they do not absorb sufficient for plant-life in the absence of other sources of moisture. The diffusion of rain in the soil depends very much on the physical condition of the soil, which for this purpose may be looked on as a mass permeated by numerous capillary tubes of smaller or larger dimensions. One important result of the experiments was the great difference in the absorptive capacity of one and the same soil when in loose or close condition, the proportion in good garden soil being in round numbers 2 : 3, and the author thinks the great advantage of deep cultivation consists as much in improving the power of absorption, as in bringing fresh soil to the surface.

J. F.

**Existence of Manganese in Plants and Animals.** By E. J. MAUMENE (*Bull. Soc. Chim.*, 42, 305—315).—Manganese occurs in small quantity in most vegetables; tea is particularly rich in manganese (0·5—0·6 per cent.). So also is tobacco, especially the Kentucky variety, which contains from 1·5—1·6 per cent. Both yellow and red-cinchona bark appear to contain more than traces of manganese. Lemons, oranges, garlic, and onions do not contain this element. Human blood, as is generally known, does not contain the metal, but

small quantities can be detected in milk, urine, bones, and hair, and in mutton fat. The fæces often contain considerable quantities, in fact the manganese taken in food appears to be eliminated principally by this excretion; whence the author concludes that manganese is not essential to the support of the animal system, and for this reason cannot be employed in medicine as a substitute for iron. It probably, however, plays an important part in the nourishment and development of certain plants.

W. R. D.

**Influence of Temperature on the Development of Wheat.** By E. RISLER (*Bied. Centr.*, 1884, 778—779).—It appears that wheat ceases to grow when the temperature falls below  $+ 6^{\circ}$ : a table shows that the highest yields have occurred in those years with the highest total temperatures (above  $+ 6^{\circ}$ ) namely:  $2215^{\circ}$  in 1868—69, and  $2318^{\circ}$  in 1873—74.

E. W. P.

**Cultivation of Swedish and German Cereals.** By G. LIEBSCHER (*Beid. Centr.*, 1884, 775—776).—Swedish seed is to be recommended for rough high lying land, but the yield of such seed is much inferior to that of German origin, except perhaps in the case of oats.

E. W. P.

**Comparison of Barleys of Different Countries.** By L. MARX (*Bied. Centr.*, 1884, 853—855).—In order to decide the question as to what country produced barley richest in proteid matter, the author analysed more than 400 samples from different countries and from harvests of six years. He found the mean percentages of proteid matter to be Russia 12·76, Baden 12·38, Sweden 11·97, Danubian provinces 11·68, Brunswick 11·49, North Germany 11·21, Bavaria 10·76, Alsace 10·70, Hungary 10·62, France 10·55, Hesse 10·43, Württemberg 10·38, Denmark 10·91 (9·91 ?), England 9·69, and Austria 9·61.

Some of the Russian barley yielded 16 per cent. of proteid matter; the maximum in Baden was 15 per cent., the minimum 10·60 per cent. Bohemia and England gave few samples of over 10 per cent.; 68 samples of Bavarian were examined, six of which were over 12 per cent., the remainder under 10 per cent.

Amongst French barleys, those of Auvergne were the lowest, those of Champagne and Burgundy being up to the average of Bavaria. The nitrogenous contents of Hungarian varied more than any other, some containing but 9 per cent., others 12 per cent.: as a rule thick skinned grain is poorer in nitrogen than thin skinned, but not invariably. The quantity of phosphates in barleys varies also within wide limits, but bears no relation to the nitrogenous contents. Chemical analysis is, in the opinion of the author, the only means of judging grain, if the brewer requires regular fermentation and sound yeast.

J. F.

**Ensilage Experiments with Various Fodders.** By KIRCHNER and others (*Bied. Centr.*, 1884, 817—822).—Experiments made in England are first referred to. Several silos at Merton in Norfolk constructed with cemented sides were filled with finely chopped coarse

grass part cut in rain, part in unsettled weather, 1—2 lbs. of salt per cwt. were added and the whole well trodden in. In one case, after three weeks, the mass had shrunk one-third in bulk, a wooden covering was then put on, then 8 or 9 inches of clay and on that heavy stones. After 3 to 5 months the fodder was found well preserved and was eaten readily by cattle, after removal of the topmost and lowest layers. Similar results were obtained with lucerne, red clover, and rye-grass. Other experiments made in Kent were equally successful. Miles (Massachusetts) in the *Milk Gazette*, recommends a method for keeping the fodder sweet, and preventing acidification. The bacteria which are the acid ferment, are killed by a temperature of 50—60°; he proposes to obtain that temperature by slow filling of the trenches, when the temperature advances to 70°; quick filling and stamping down will only give about 40°. Baker is reported to have used old petroleum barrels as silos and kept fodder therein for a long time, without injury. Thomas, who reports on these experiments, thinks there is nothing new in them, and that they teach nothing; he considers it is teaching a false doctrine to say that green fodder can be preserved unaltered; heating more or less must take place, which in a plant is a sign of decay, and fermentation must invariably set in, attended with important loss of substance.

Kirchner as a result of his experiments expresses an unfavourable opinion of ensilage with green maize; there was a loss of 15 per cent. in weight, of which about one-third was protein, and in 8 months there was a loss of 41.2 per cent. of protein. In three experiments, in feeding milch cows with acid fodder, he found that the quantity of milk was increased, but the quality deteriorated, there was less fat, it had the taste of butyric acid, and the butter made from it kept badly and had a disagreeable flavour. Schultze studied the changes which took place in lupines, maize, and lucerne preserved in casks for three months, at the end of which time a very serious loss of nitrogenous substance had occurred. E. Kinch, in experiments with grass perceived a similar loss (*Trans.*, 1884, 122); Liebscher made experiments with sliced beets in deep trenches lined with cement, and covered some with heavy stones, some with soil; in two of them 1 kilo. of borax was mixed with the roots. In six trenches, the percentage of weight lost was from 7 to 19 per cent., and the addition of borax appeared to have an injurious effect. J. F.

**Loss of Weight in Ensilage of Beet-leaves.** By M. MÄRCKER (*Bied. Centr.*, 1884, 815—816).—Two quantities of leaves were stored in pits in October, and taken out in March: the loss per cent. on one lot was 16.31, on the other 16.38, the analysis showed that part of the protein had changed to amides, lowering the value as fodder.

These experiments convince the author that acidification of green fodder is a wasteful operation, only to be resorted to when other methods of preservation are not possible, as is often the case where large crops of beets are grown. J. F.

**Cultivation of Sugar-beet at Grignon in 1884.** By P. P. DEHÉRAIN (*Ann. Agronomiques*, 10, 529—539).—The experiments of

1884, were undertaken with the especial object of ascertaining to what extent certain improved strains or varieties of sugar-beet would withstand the impoverishing effect (as regards percentage of sugar) of heavy doses of farmyard dung and other nitrogenous manures. The variety chosen was "Vilmorin's improved" sugar-beet, with which the author had previously obtained excellent results as regards yield. The weight of roots and leaves obtained on the different plots, and the percentage of sugar contained in the juice, are set forth in the annexed table:—

Manure per hectare.	Roots, kilos.	Leaves, kilos.	Sugar, per cent. of juice.
30,000 kilos. farmyard manure + 300 kilos. sodium nitrate .....	43,400	27,400	18·1
20,000 kilos. farmyard manure + 400 kilos. sodium nitrate .....	36,000	20,500	17·6
30,000 kilos. farmyard manure + 1500 kilos. lime .....	35,900	17,000	17·4
20,000 kilos. farmyard manure + 200 kilos. sodium nitrate + 200 kilos. potassium chlo- ride .....	38,000	20,000	18·9
20,000 kilos. farmyard manure + 500 kilos. flesh manure .....	33,400	14,600	19·4
40,000 kilos. farmyard manure .....	35,500	13,700	18·8
40,000 kilos. farmyard manure + 200 kilos. sodium nitrate .....	38,200	14,200	18·0
1000 kilos. flesh manure .....	33,200	13,200	19·2
1000 kilos. flesh manure + 1500 kilos. lime ..	30,700	14,700	17·8
500 kilos. torrefied horn .....	33,700	12,300	19·6
1000 kilos. new leather, torrefied .....	34,900	13,100	18·7
1000 kilos. old leather, torrefied .....	31,300	11,100	19·8
800 kilos. azotine .....	34,200	16,500	19·4
1000 kilos. "beet manure" .....	34,200	16,000	20·4
1000 kilos. "phosphoguanos" .....	33,600	13,900	19·9
Unmanured .....	29,700	—	19·0

*Azotine* is a soluble nitrogenous manure prepared by the action of alkalis on woollen and cotton refuse.

The most suitable manure appears to be farmyard manure in conjunction with Chili saltpetre; the results of the experiments of previous years lead also to this conclusion. The variations in the percentage of sugar are so small that they cannot be attributed to the action of the different manures; on the other hand, the experiments show that a suitably chosen seed will respond liberally to large dressings of manure without any deterioration in the quality of the roots. Analyses of roots taken at random showed also that the large roots were as rich in sugar as the small ones.

J. M. H. M.

**Cultivation of Various Sugar-beets.** By G. LIEBSCHER (*Bied. Centr.*, 1884, 774—775).—When manured with 18 per cent. super-phosphate and Chili saltpetre, "Little Wanzlebener" yielded best as

regards total weight of roots and sugar, though "*Vilmorin blanche*" gave the highest coefficient of purity. At an experimental station 400 feet higher, the results as regards yield were the same, but the richest roots were produced from Stroebnitz seeds. E. W. P.

**Sugar-beet Seed as Fodder for Cattle.** By H. PELLET (*Bied. Centr.*, 1884, 755—756).—Old sugar beet seed is recommended as a valuable substitute for linseed cake; by its use, cattle will increase at the rate of 1·57 kilo. daily. E. W. P.

**Adulteration of Linseed Cake and Rape Cake.** By G. KLEIN (*Bied. Centr.*, 1884, 788).—Chaff and water are now being largely added to linseed cakes. In rape cake, the unground seeds of *Setaria viridis* and other plants have been found, all of which are almost absolutely indigestible. E. W. P.

**Composition of the Seeds of the Cotton Tree.** By SACC (*Compt. rend.*, 99, 1160—1161).—The seeds of the cotton tree cultivated in Bolivia have the following composition:—Casein 6·00; dextrin 0·20; sugar 2·0; fibrin 23·70; lignose 32·40; starch 9·60; oil 9·60; wax 0·80; ash 8·00; water 8·00 = 100. They yield when ground, yellow flour 56·50; black bran 40·50; loss 3·00 = 100. It is evident that these seeds may constitute a very valuable food. A solution of the seeds may be used for removing the excess of lime employed in sugar refining, the lime being precipitated in the form of an insoluble caseate. The aqueous solution also forms an agreeable orgeat. C. H. B.

**Analyses of Cotton Seeds.** By F. KÖNIG (*Bied. Centr.*, 1884, 791).

	American. per cent.	Egyptian.	
		Natural. per cent.	Freed from cotton. per cent.
Water .....	9·24	10·78	11·42
Albuminoids .....	16·88	19·50	19·94
Fat .....	14·86	24·76	25·34
Non-nitrogenous extrac- tive .....	28·12	20·63	20·08
Fibre .....	27·60	20·13	18·93
Ash .....	4·30	4·18	4·29

E. W. P.

**Fairy Rings.** By F. v. THÜMEN (*Bied. Centr.*, 1884, 792).—These rings are produced by the growth of mycelium, which contains much nitrogen, so that the grass receives much valuable manure. At the same time this fungus exerts a baneful influence on the grass roots, consequently discolored grass is frequently to be found within the ring. E. W. P.

**Variations in Rainfall.** By W. KREMSEK (*Bied. Centr.*, 1884, 793—794).—The author has had the opportunity of collating the results of an extended series of observations made under the auspices

of the Italian Meteorological Institute at 15 Italian and 24 German stations, with a less number of those in other countries. He states that the variations in the amount of rainfall increase as the equator is approached, and that regions lying under the shadow of mountain ranges are more subject to alterations than plains in the same latitude. The mountains arrest the rain clouds, but the distances of those clouds from the earth of course affects the results. In plains, the fall is more regular. The variations are greater in cold seasons of the year than in the warm months. J. F.

**Micro-organisms in Soil.** By E. WOLLNY (*Bied. Centr.*, 1884, 796—814).—The changes, physical and chemical, which take place in earth containing humus, or the organic remains from which it is formed, are of great interest, and have important bearings on the fertility of the soil. In well-worked porous and aerated ground, the decomposition of organic matter under favourable conditions liberates carbonic anhydride, water, ammonia, and a little free nitrogen, some of which combine with the inorganic substances necessary for the growth of the plant. The process of decomposition is generally considered as one of oxidation, and Schlösing, Müntz, and Warington regard it as due to the action of lower organisms. In well aerated soils, little ammonia is formed; it is quickly oxidised to nitric acid; but when the nitrifying organism is destroyed by treatment with chloroform, carbon bisulphide, or by means of heat, the ammonia prevails, and the nitrites and nitrates are reduced. Schlösing and Müntz produced nitrification in sterilised solutions by the addition of a mere trace of earth; they found in the fluid small filiform bodies, from which pure cultures were obtained. This they consider to be the nitric ferment; it is widely diffused, and finds its most favourable habitat in arable soils; it is also found in sewage water, and less frequently in flowing water; it does not appear to exist in the air, at least it has not been obtained from that source.

It is easy to understand the great influence exercised by conditions of moisture, heat, and light on the activity and multiplication of these organisms. Schlösing proved in 1873 that nitrification depends on the free access of oxygen; when the supply is restricted, nitrification ceases, and when it is withheld altogether, the nitrates already formed are reduced. Moisture is also an important factor; even at ordinary temperatures dryness is hurtful to the ferment, and earth in which the process is in full activity is rendered perfectly sterile by being dried. It is not surprising that heat should greatly influence the growth of the ferment; at 5° the process proceeds slowly; at 12° it is clearly visible; at 37° it reaches its maximum, and at 55° it ceases. Warington's experiments (*Trans.*, 1878, 44) have shown the great influence of light, the organisms prospering best in darkness.

The oxidation of the carbon of organic matter is caused in a similar way by organisms, and under conditions very similar to those of nitrification. The author has established that treatment with chloroform vapour, the addition of antiseptics such as carbolic and boric acids, or thymol, or heating to 130°, very materially retards the production of carbonic anhydride. The same factors which promote nitrification

influence this process; the production of carbonic anhydride proceeds at the same time as nitrification, but is independent of atmospheric oxygen, deriving what is required from the soil. This appears to support the opinion that the air contained in well tilled soil is frequently changed. It is well known that organic substances used as manures decompose more rapidly in well aerated earth, sandy or gravelly, than in close, loamy, or argillaceous soil. Warmth greatly influences the activity of production; the most favourable temperature is  $50^{\circ}$  to  $60^{\circ}$ , but even at  $0^{\circ}$  the process goes on slowly. Moisture is in this case as necessary as in that of nitrification; soil containing 4 per cent. of water was found by Fodor to yield 16 times as much carbonic anhydride as the same soil with only 2 per cent.; too much moisture arrests the process by diminishing the quantity of available oxygen present. The reduction of the nitrates already formed must be considered also as a physiological process, dependent on the presence of organisms which do not require oxygen (Pasteur's anaerobes). Deprived of air, the organic matters yield small quantities of carbonic anhydride, water, ammonia, free nitrogen, and a carbonaceous, black, turf-like mass, an acid humus, difficult of decomposition. Recently, a ferment has been discovered in arable soil which is capable of inducing alcoholic fermentation. The enormous numbers of micro-organisms in soils may be guessed from observations made at the Observatory of Montsouris, where one gram of earth was computed to contain 750,000, and at Gennevilliers, 870,000 to 900,000 spores.

As the influence of heat, moisture, &c., does not always tend in the same direction, the author believes that the decomposition of organic matter is governed chiefly by that factor, of which a minimum is present. The physical conditions of soils have a very great influence on decomposition, namely, permeability to air, the capacity to retain moisture, and in great measure the state of the subsoil. The power of absorbing and retaining the sun's heat is different in various soils; a dark-coloured soil is warm during the day, and parts quickly with its heat at night. This variation can, however, be fully neutralised by judicious admixture of humous substances.

The effects of vegetation and of spreading manures, straw, &c., on the surface are very important; ground when protected by vegetation is warmer than when fallow, and variations of temperature are less; when covered with a thin layer of straw, &c., it is a medium between naked and vegetation-covered soil; if the layer is too thick, it becomes colder. In speaking of the effects of the constant culture of food plants, the author comes to the conclusion that soils which are tilled year after year become poorer, no matter how richly they may be manured, and that they commence to recover their fertility when laid down in grass for either meadow or pasture. This property of enrichment of the soil belongs also to leguminous plants, but it is not because, as many assert, that these plants have the power of obtaining nitrogen from the atmosphere, but is due altogether to the methods of culture.

The chemical composition of soils has an important bearing on the decomposition of organic matter; the presence of lime facilitates it greatly; the contents in humus is also a factor; the production of carbonic anhydride does not proceed always at as rapid a rate as at



first, and too great a quantity may hinder the activity of the micro-organisms. The author considers the subject one for further experiment, but is of opinion that no doubt should exist that all changes in the humous matters contained in arable earths are due to micro-organisms, and that their activity is governed by the factor which is present in a minimum, and is dependent on a balance of various important influences. J. F.

**Germination in Soil rich in Organic Matter, but free from Microbes.** By E. DUCLAUX (*Compt. rend.*, 100, 66—68).—Haricot beans and peas were sown in soil which had been previously sterilised, and then moistened with sterilised milk, care being taken that no microbes were introduced along with the seeds. Under these conditions the seeds germinated, but after two months the milk had undergone no alteration, and the plant when dried weighed less than the original seed, and in appearance resembled the plants produced by the germination of seeds in distilled water. The author has previously shown that casein only becomes assimilable by living organisms under the simultaneous or successive action of two diastases, rennet and casease. It would seem, therefore, that the seeds in germinating do not secrete and diffuse through the surrounding soil either of these diastases. Precisely similar results were obtained with soil containing saccharose, and with soil containing starch-paste. The cotyledons, therefore, secrete neither sucrase nor amylase.

These results show that a seed germinating in a soil rich in organic matter is unable of itself to assimilate the organic matter, and is dependent on the action of microbes which convert the organic matter into assimilable forms, and thus place it at the disposal of the plant.

The fact that a germinating seed cannot assimilate starch from the surrounding soil, seems at first sight opposed to the fact that the reserve store of starch in the seed itself is used up during the germination of the seed and growth of the young plant. For a plant to secrete diastase in the interior of its own tissues is, however, a very different thing to diffusing it into the surrounding soil.

C. H. B.

**Solution of Wool-dust.** By MÄRCKER (*Bied. Centr.*, 1884, 785).—For every centner of wool-waste, 5—7 kilos. calcium oxide is to be slaked and mixed with the wool, thoroughly moistened with water and mixed so as to remove all fat; the heaps, 6 inches high, are to be left covered with earth for two to three months, but they must be kept moist. After this time an excellent compost is formed. Sulphuric acid may also be used; it is more expensive, but there is then no loss of ammonia. The mixture of wool and 50° acid is made in leaden troughs, and regularly stirred until the mass becomes thick and unworkable.

E. W. P.

**Peat as Manure.** By SCHREINER (*Bied. Centr.*, 784).—Oats were sown in boxes filled with sand, to which had been added various mineral manures, and in some cases 5 per cent. of peat. The best crops were obtained from minerals (no details given) and ammonium

sulphate and peat; the same results were obtained when barley, rye, beans, &c., were grown.  
E. W. P.

**Straw, Peat, and Sawdust as Litter.** By H. SAGNIER (*Bied. Centr.*, 1884, 783).—These three materials were employed by the Paris Omnibus Company as litter, and there was produced of straw manure 25 kilos., of peat 10—11, of sawdust 12—13 kilos. per horse daily, and they contained 0·51, 0·68, and 0·45—0·49 per cent. N respectively. After use on the land as manure for two successive crops, it was found that the sawdust and peat were equally good, and both of them better than straw.  
E. W. P.

**Manuring Experiments with Precipitated Phosphate.** By LÖBBECKE (*Bied. Centr.*, 1884, 735).—The crops were barley after beet, oats after potatoes; and the manures Chili saltpetre, saltpetre with superphosphate, and with precipitated phosphate. Results: the nitrate increased the crops, and the addition of superphosphate was of no advantage, but precipitated phosphate was a gain; the land where the barley was sown was clayey loam, whilst the oats grew on chalky humous soil.  
E. W. P.

**Sidney Guano.** By MÄRCKER (*Bied. Centr.*, 1884, 785).—This is a new guano from Sidney Island resembling Baker Island guano, and produces 18·8 per cent. soluble phosphate. Gilbert's analysis is as follows:—Water 7·38, CO<sub>2</sub> 2·64, SO<sub>3</sub> 1·63, P<sub>2</sub>O<sub>5</sub> 34·41, CaO 42·96, MgO 2·03, Na<sub>2</sub>O 0·76, Cl 0·87, Fl 0·40, organic matter 7·29 (N=0·28).  
E. W. P.

**Manuring Sugar-beet.** By G. LIEBSCHER (*Bied. Centr.*, 1884, 737—745).—It was arranged that phosphoric acid should be tried against nitrogen (equal quantities of Chili saltpetre and ammonium sulphate) and against farmyard manure in various proportions, and well mixed with one another. During growth, those plants were the strongest which were manured with nitrogen and farmyard manure, phosphates having but little influence by reason of the drought. The heaviest crop both of roots and sugar was produced by the use of 800 centners farmyard manure, mixed with 72 kilos. per hectare of phosphoric acid in the form of 18 per cent. superphosphate. This same result was obtained when equal parts of nitrogen and phosphate were used. The author then discusses the quantities of each manure which are most beneficial from a financial point of view on his land, as well as the value of farmyard manure under the same circumstances.  
E. W. P.

**Parallel Experiments on Peat Compost and Chili Saltpetre as Manures for Sugar-beet.** By L. KUNTZE (*Bied. Centr.*, 1884, 745—747).—The compost which is obtained by soaking up the waste liquids from the sugar manufactory with peat contains 2·5—3·3 per cent. N, and 11·5—14 per cent. K<sub>2</sub>O, and it is in a good saleable form. This compost was compared with saltpetre as a manure, both being aided by guano or superphosphate. Taking the average of the

plots, the peat compost was the best both as regards total yield and "quotient of purity." Several varieties of roots were sown, but all with a similar result.

E. W. P.

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## Analytical Chemistry.

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**Estimation of Hydrogen Peroxide.** By H. S. CARPENTER and W. O. NICHOLSON (*Analyst*, **9**, 36—41).—The authors have made numerous determinations of the quantity of hydrogen peroxide in aqueous solutions, employing various methods—titration with  $\frac{N}{10}$  permanganate and measurement of the volume of gas liberated, and titration with potassium iodide and sodium thiosulphate. From their results, they conclude that the reaction which takes place when an acid solution of hydrogen peroxide is treated with permanganate, can be correctly represented by the equation  $K_2Mn_2O_8 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$ , as stated by Kingzett (*Trans.*, 1880, 805). Moreover, they recommend the first of the above-mentioned methods as rapid and accurate, and remark on the inferior quality of commercial hydrogen peroxide. D. A. L.

**Apparatus for the Rapid Estimation of Hydrogen Peroxide.** By MARTINON (*Bull. Soc. Chim.*, **42**, 449—451).—A small wide tube or flask is fitted with a caoutchouc cork with two holes, through one of which connection is made with an open graduated tube, of which the lower end is immersed in water; through the other passes a tube closed at its upper end and blown out to an open bulb at the lower extremity, in such a manner as to hold a few drops of liquid. 1 or 2 c.c. of the hydrogen peroxide are placed in the wide tube, and a fragment of manganese dioxide with three or four drops of solution of caustic soda, potash, or ammonia (free from carbonates) in the small bulb. The latter, after the cork has been firmly fixed, is pushed down into the hydrogen peroxide, the solution shaken, and the amount of oxygen generated is read off in about two minutes, the usual precautions being observed. J. K. C.

**New Method of Testing for Chlorates.** By FOURMONT (*J. Pharm.* [5], **10**, 96—97).—A solution of a chlorate when treated with copper and sulphuric acid gives a green solution; a nitrate similarly treated gives a blue solution. If chlorides and nitrates are both present, the former must first be removed by precipitation with silver acetate. H. B.

**Quantitative Estimation of Nitrogen.** By K. KREUSLER (*Land. Versuchs-Stat.*, **31**, 207—318).—After stating his objections to Dumas' method for the volumetric estimation of nitrogen, as

occupying much time, being troublesome and expensive, the author proceeds to describe the modifications which he has introduced, so as to render the analysis more accurate, more rapid, and less extravagant. The first object to be attained is that the whole apparatus shall be free from air, and that when oxygen and carbonic anhydride are introduced, there shall be no air introduced at the same time. The ordinary method for the preparation of carbonic anhydride, by the action of hydrochloric acid on marble, is unsatisfactory, as there is always a residue of air amounting to  $\frac{1}{1000}$  of the volume of the apparatus; the production of carbonic anhydride by the heating of sodium hydrogen carbonate, lead or manganese carbonate in auxiliary tubes, is likewise unsatisfactory, for although pure gas is formed, yet it is at the risk of destroying the whole analysis. The employment of combinations of these two processes, as recommended by Ritthausen (*Pflüger's Archiv*, 18, 336) and Gruber (*Zeit. f. Biol.*, 16, 371), is followed by good results, but the simplicity of the whole arrangement is much impaired.

It is therefore recommended that carbonic anhydride should be prepared from sodium carbonate and sulphuric acid, when gas containing only  $\frac{1}{5000}$  of air is produced. Whilst working at this part of his researches, the author found that there were no exact accounts of the quantity of air set free by the action of hydrochloric acid on marble, consequently he experimented on this point, and found that as a rule 1 litre of carbonic anhydride contained  $\frac{1}{2500}$  of its volume of air; when sulphuric and sodium carbonate were employed, the admixture was reduced to  $\frac{1}{4700}$ , and even to  $\frac{1}{6000}$ , when the soda was very compact and the acid freshly prepared. To prepare the sodium carbonate in the best form for use, it is fused with  $\frac{1}{3}$ — $\frac{1}{5}$  of pure potash, and cast in small sticks; the acid consists of 2 vols. concentrated acid, which is to be added to 3 vols. of boiling water; if the acid is introduced slowly at the edge of the basin the whole mixture is kept at the boiling point, and when cooled it will absorb but little air. A further source of error is the air which obstinately adheres to the surface of the combustion tube, asbestos, copper oxide, and finely divided copper, but still, this small quantity may be nearly wholly got rid of by removal of the air and introduction of carbonic anhydride, but such is not the case when granular copper oxide is employed. To avoid this residual air as much as possible, granular copper oxide should not be used if it can possibly be replaced by anything else, but if otherwise the exhaustion of the whole apparatus is imperative, as well as heating the oxide. On account of these objections to the use of copper oxide, copper oxide asbestos and copper asbestos are recommended as far superior to any of the three used separately, because it is quite possible for hydrocarbons to escape combustion by passing through channels in the copper oxide, without coming in direct contact with it; the elasticity of the copper oxide asbestos prevents the formation of these channels, and consequently no hydrocarbons can escape as such. Copper oxide asbestos is prepared as follows:—Dissolve 150 grams of copper sulphate in 400 grams hot water, plunge into this solution 50 grams of loose asbestos of medium length of fibre, and then evaporate the mixture nearly to dryness; place the

asbestos thus saturated with salt in a dilute sodium hydroxide solution (160 grams to 2—3 litres water), and boil for half an hour, or until the liquid is no longer coloured blue or green, then decant, collect the solid on a filter and wash until all sulphuric acid is removed; after drying, and before immediate use, ignite in a crucible. When the copper asbestos is required, the above preparation is reduced in an ordinary combustion-tube, and to facilitate the passage of the gas, a cylinder of wire is first introduced, which cylinder may afterwards be filled with the asbestos. As a frequent consequence of incomplete combustion, the percentage of nitrogen is found to be too low; this is generally obviated by the employment of mercuric and silver oxide, but for various reasons the author objects to the employment of these and most other compounds which set free oxygen when heated; he prefers to generate oxygen from a mixture of potassium chlorate with  $1\frac{1}{2}$  times its volume of copper oxide. To ensure a quiet and regular evolution of gas, the chlorate should be fused, cooled, and powdered, and then carefully mixed with the exact quantity of the copper oxide, preferably by shaking it thoroughly in a flask.

Another source of error in analysis is the passage of unreduced oxides of nitrogen out of the combustion-tube; to insure the reduction, metallic copper, in the form of a spiral of turnings, &c., is generally introduced into the tube; Kreusler, however, prefers to use the copper asbestos already referred to, as he finds that all oxides are reduced, and, however rapid may be the evolution of oxygen, none ever passes the plug of asbestos. Morgan (*Zeit. Anal. Chem.*, **21**, 253) has stated that a further source of error is the formation of nitric and nitrous acids (nitric oxide oxidised by oxygen), which attack the glass of the combustion-tube, forming their corresponding salts; but this statement the author has been unable to confirm. The author deplores the care with which analyses are calculated out to the second and third decimal place, when it is remembered how little attention is paid to other factors which should be considered in the calculations, namely, that burettes, &c., are not always calibrated, that no account is generally taken in weighing of the value of the displaced air, &c.

The method of analysis is described at great length with the aid of diagrams in the original paper, and does not admit of abstraction, a short statement of the arrangements in the combustion-tube must therefore suffice. The combustion-tubes should be about 115 cm. long by 14 mm. broad, both ends being open and with rounded edges, and at about the middle of the tube a plug of copper oxide asbestos, about 2 cm. long, is to be inserted; to the left of this comes about 2 cm. of granular copper oxide, and then about 24 cm. of copper oxide asbestos. The next 14 cm. is occupied by metallic copper, the first 2 cm. consisting of compact metal produced by oxidising turnings and then reducing them, whilst the last 12 cm. is filled with copper asbestos; finally, 6 cm. are occupied by copper oxide asbestos. Previous to the filling of the tube in the manner just stated, a copper wire spiral is introduced, extending the whole length thus filled. The boats for holding the substance and the potassium chlorate are made of sheet

brass, worked into shape round a glass rod; the boat which holds the substance is placed in the middle of the tube, and is separated from the other boat at the end by a cylinder, 10 cm. long, of platinum gauze, containing copper oxide asbestos; this cylinder is furnished with a short wire bent into a loop, so as to be readily withdrawn. To prevent bursting from internal, or collapsing from external pressure, the whole tube is enveloped for four-fifths of its circumference in sheet brass divided into five pieces, which overlap one another at their junctions, where they are lightly bound round the tube by wire; the whole is then laid on the bed of the furnace, which has been previously strewn with talc or magnesite. With the apparatus so constructed, several analyses may be made, as only the boats and the platinum cylinder have to be withdrawn for refilling and removal. The connection between the combustion-tube and the other parts of the apparatus are made by short pieces of glass tubing fixed into the combustion-tube by short pieces of india-rubber tubing; these glass slips, which are somewhat tapered at the end, pass into conical tubes, which are connected respectively with the carbonic anhydride apparatus and the gas measurer; to ensure hermetic closing at the junction of the two glass tubes, sealing-wax is used as proposed by v. Jolly. The capillary tube leading from the carbonic anhydride apparatus is of copper, whilst the glass tube leading to the gas measurer rises upwards for a height of over 76 mm., the supports employed do not press on any part of the whole arrangement, no clamps being used. For the method of conducting the combustion, of collecting the gas and its measurement, reference must be made to the original paper. The small amount of air which persistently adheres to the metallic copper, and is not removable by exhaustion nor by carbonic anhydride, has been already referred to; to remedy this error 0.13 mgrm. N must be subtracted from the total nitrogen for every 5 grams of metallic copper employed. Estimations of nitrogen in various organic and inorganic compounds are given to show the accuracy of the process which, for its performance, only requires about 100 minutes.

I. *Experiments with Will-Varrentrapp's Method and some Remarks on Kjeldahl's Process.*—The estimation of the nitrogen in many nitrogenous compounds, such as uric acid, legumin, &c., when made by the soda-lime process, is quite accurate, but there are some substances which, as Liebermann and others have shown, do not yield up the whole of their nitrogen in the form of ammonia. Menozzi asserts that he can only obtain 40 per cent. of the nitrogen in milk as ammonia; Musso says that when milk has been creamed it will only give up 81–88 per cent. of its nitrogen. Kreusler therefore has made analyses of milk under various conditions, employing in some cases a glass tube, in others a short or a long iron tube, mixing the dry milk with chalk, &c., both dry and moistened with water. The mixture of the substance with some neutral solid is placed in a boat of sheet iron 25 cm. long, when it is well moistened and thoroughly mixed with soda-lime. The results obtained were as follows:—The addition of indifferent substances (calcium carbonate, strontium sulphate) to the dried milk did not raise the percentage of nitrogen

above 90 per cent. of the whole nitrogen present; if moist hydrogen was passed through, then the yield was raised to 93—95 per cent., and finally the use of an iron tube again brought a slight increase.

As Will-Varrentrapp's method was found to be so untrustworthy, Kjeldahl's method (*Zeit. Anal. Chem.*, **22**, 366) was examined to see whether it really was an improvement, and also whether it could be improved upon. To prepare a strong acid in which to digest the substance to be analysed, 1 litre of rectified sulphuric acid was mixed with 200 grams of phosphoric anhydride; 20 c.c. of this acid is quite sufficient to act on 1—1.5 gram substance. The digestion was conducted in a flask slightly inclined, and partially closed, the heat being applied for six hours; the addition of the permanganate was without danger. To drive off the ammonia, 100 c.c. of soda solution (1 part of fused sodium hydroxide to  $2\frac{1}{2}$  parts water) was added, and the mixture boiled over a naked flame in a globe-shaped flask, the level of the liquid being kept constant (the amount of liquid being about 250 c.c.); the introduction of zinc turnings permitted the evaporation to be carried on until the volume was reduced to 150 c.c., before any "bumping" set in. Even with these special precautions, the albuminoids of milk resisted the conversion, if the digestion was only carried on for three hours, and conversion was only completed when digestion had lasted six hours. Great care must be exercised in examining the "pure" sulphuric acid and the permanganate for nitric acid, for both frequently contain a small percentage.

*Estimation of Nitrogen as Amides, &c., by Means of Nitrous Acid.*—Sachsse and Kormann's process (*Land. Versuch-Stat.*, **17**, 88 and 321), in which the amide compound is treated, was put to the test, as also the various absorbents of nitric oxide recommended by Böhmen and others. A full description of the author's process cannot be given without diagrams. The acid employed was pure, and was diluted with boiled water; the potassium nitrite must be purified by double decomposition with calcium nitrate, as there is always carbonate present. The solution of ferrous sulphate is prepared by first moistening the crystals with sulphuric acid, and then dissolving them so as to form a saturated solution. Even with all the precautions which were used, a blank experiment showed that for every 10 c.c. of nitrite solution containing 7.18 grams salt, there were produced and passed into the receiver 3 mgrms. of nitrogen. This quantity has been employed as a correction in the analyses which are described; the source of this error has not been discovered. Should any carbonic anhydride pass off with the nitric oxide and nitrogen, it will be absorbed by the ferrous sulphate, as experiments have shown that 200 c.c. of this solution can absorb 2.79 c.c. of the gas. Analyses of tyrosine, asparagine, leucine, and aspartic acid, alone, or when mixed with a nitrate, do not yield the true amount of nitrogen present, in some cases the yield was too high, in others much too low; even when the substances were treated with dilute acid and a base, the results were no better, but it is hoped that further researches will enable correct estimations to be made. The apparatus and experiments made to obtain exact results by the action of nitrous acid and long continued boiling are fully detailed, but no results were obtained which were perfectly trustworthy; the best



determinations were made when the substance was treated with the acids for a long time at a high temperature. Collecting, out of the immense amount of detail, the results of the experiments on individual compounds, we find that the analysis of urea comes out higher, the longer it has been heated with dilute acid previous to the action of the nitrous acid. Leucine seems to decompose completely under the circumstances. Allantoin requires a long and energetic action of the acids before it is completely decomposed, and before it yields up all its nitrogen; the nearest approach to absolute correctness was 99.5 per cent. N, when 7.2 grams potassium nitrite had been used, and the heat applied for 30 hours. Caffeine and quinine are not decomposed. Uric acid, which under the influence of fuming nitric acid gives up  $\frac{1}{4}$  of its nitrogen, loses 40 per cent. under the conditions of these experiments. Hippuric acid loses half its nitrogen after 14 hours previous heating, amidobenzoic acid (meta-?), tyrosine, and aniline oxalate, yield respectively three, five, and three and a half times the proper amount of nitrogen. The author accounts for these results by supposing that with these aromatic compounds nitroso- or diazo- compounds are first formed, which, afterwards decomposing, produce the excess of nitrogen observed; this supposition is supported by the fact that pure phenol when treated in like manner yielded a large amount of nitrogen.

*Schlösing's Process for estimating Nitric Acid.*—Against this process as conducted in his apparatus, the author has nothing to say. For the collection of the nitric oxides, he employs a 7 per cent. solution of sodium hydroxide, sp. gr. 1.075; the vapour-tension of this solution differs from that of water by a mean quantity of 1.4 mm. mercury, at 20°. The presence of amido-compounds (asparagine) and other organic compounds, such as sugar, have but little influence on the accuracy of the analysis.

E. W. P.

**Estimation of Nitrogen in Chili Saltpetre, &c.** By P. WAGNER (*Chem. Centr.*, 1884, 475).—The method described is a modification of Schlösing's method. A flask of about 200 c.c. capacity is provided with an india-rubber stopper, fitted with a dropping funnel and an exit-tube dipping under water. 40 c.c. of a solution of ferrous chloride (containing 200 grams iron in a litre) are introduced, the air expelled from the apparatus by boiling, and then 10 c.c. of a normal solution of sodium nitrate (containing 33 grams sodium nitrate in a litre) added, the dropping funnel being twice rinsed into the flask with 20 per cent. hydrochloric acid; the nitric oxide evolved is collected in a 100 c.c. measuring tube, and when the evolution ceases, 10 c.c. of the solution of the nitrate to be examined are added, and the gas is collected in a fresh tube. In this way, six or seven estimations may be made without renewing the ferrous solution, which is of course kept boiling the whole time. The tubes are surrounded by water, in order to bring them to a uniform temperature, and the volumes noted; the calculation is simple, as no allowance has to be made for temperature and pressure.

A. K. M.

**Nitrogen in Artificial Manures.** By J. OSTERSETZER (*Chem. News*, 50, 291).—The following experiments were made, in order to get some idea of the theoretical value of the methods now employed for the determination of the relative value of nitrogen from various manurial sources. The four kinds of manure enumerated in the table were treated respectively with water, with large excess of ammoniacal solution of ammonium citrate, with rectified sulphuric acid, sp. gr. 1·85, and with a boiling concentrated solution of citric acid. In each case, a separate weighed quantity of the fresh material was employed, and the nitrogen determined in the various insoluble residues. The following table is constructed from these results:—

Manure.	Nitrogen, per cent.	Percentage of nitrogen.				
		Soluble in				Insol. in
		Water.	Amm. citrate.	Citric acid.	Sulph. acid.	Sulph. acid.
Peruvian guano . . . .	5·88	64·27	18·71	4·59	9·88	2·55
Dried blood (at 100°)	15·91	14·77	14·59	25·00	40·55	5·09
Bone meal . . . . .	3·50	2·86	1·43	8·57	75·71	11·43
Wool waste . . . . .	9·12	0·00	0·00	61·41	24·44	14·15

The sulphuric acid evidently renders a large quantity of the nitrogen in organic substances soluble. The same four manures were then destructively distilled; the results as regards nitrogen are tabulated below:—

Manure.	Percentage of nitrogen.		
	Evolved as		Left in the char.
	NH <sub>3</sub> .	N.	
Peruvian guano . . . . .	83·33	14·27	2·40
Dried blood . . . . .	47·58	39·23	13·19
Bone meal . . . . .	48·00	42·00	10·00
Wool waste . . . . .	53·73	30·92	15·35

D. A. L.

**New Method of Determining Phosphoric Acid in Manures.** By G. L. SPENCER (*Chem. Centr.*, 1884, 445—446).—5 to 20 grams of the manure are ignited until the ash becomes white, the latter is then boiled with strong nitric acid, diluted, filtered, and the residue washed. In this manner, the greater part of the iron is separated, and the

chlorides are decomposed. The filtered solution is made up to a definite volume, and of this a certain quantity is taken so as to contain from 0.1 gram to 0.5 gram phosphoric acid. To this portion, a slight excess of silver carbonate is added, a perfectly insoluble precipitate of silver phosphate being at once formed. After boiling and filtering, the precipitate is thoroughly washed with boiling water, and then dissolved in a minimum quantity of dilute nitric acid. The silver is precipitated from this solution by means of sodium chloride, and after neutralising with sodium carbonate, the phosphoric acid is determined by means of standard uranium solution. The method appears to be accurate, rapid, and inexpensive. P. F. F.

**Estimation of Phosphoric Acid in Manures. Methods adopted for 1885, by the Association of Official Agricultural Chemists** (*Chem. News*, 51, 19).—*Phosphoric acid soluble in water.*—2 grams of the well sampled manure are washed with water on a filter until the washings are nearly free from phosphoric acid, the substance is then rubbed to a paste in a mortar with a pestle tipped with rubber, and re-washed until the washings are free from acid. The phosphoric acid is determined in the mixed washings, as described below.

*Phosphoric Acid Insoluble in Ammonium Citrate.*—The residue and filter-paper from the water treatment are digested with 100 c.c. of neutral ammonium citrate solution (density 1.09), at 65°, for 30 minutes, with frequent shaking, then filtered, washed, and ignited until organic matter is destroyed; the residue digested with 10–15 c.c. of fuming hydrochloric acid, until the phosphate is dissolved, diluted to 200 c.c., filtered through a dry filter, and the phosphoric acid estimated, as described below.

*Total Phosphoric Acid.*—2 grams of substance are well mixed with 4–7 c.c. of a nearly saturated solution of magnesium nitrate, dried and ignited until free from organic matter. The phosphoric acid is dissolved out by digesting this residue at a gentle heat with 15–20 c.c. of fuming hydrochloric acid; the solution is diluted to 200 c.c., and passed through a dry filter. 50 c.c. of this or of the preceding filtrate, or  $\frac{1}{6}$  to  $\frac{1}{4}$  of the washings referred to above, are neutralised with ammonia, mixed with 15 grams dry ammonium nitrate, and precipitated with molybdic solution, digested at 65° for one hour, filtered, and washed with ammonium nitrate solution. The filtrate should be tested with molybdate for phosphoric acid; the precipitate is dissolved in ammonia and hot water, nearly neutralised, cooled, and magnesia mixture is run in at the rate of a drop per second (comp. Lindo, *Abstr.*, 1884, 494) with vigorous stirring; after 15 minutes 30 c.c. ammonia sp. gr. 0.96 are added, and in two hours the mass is filtered, washed with dilute ammonia, ignited, and weighed.

*Phosphoric acid soluble in ammonium citrate* is the difference between the total, and the sum of the phosphoric acid soluble in water, and that insoluble in ammonium citrate.

The reagents are prepared as follows:—*Ammonium citrate.*—Commercial citric acid is dissolved in water, nearly neutralised with ammonium carbonate, the carbonic anhydride boiled off, the neutralis-

ing completed with ammonia, and the solution diluted until its sp. gr. is 1.09. *Magnesium nitrate*.—320 grams of calcined magnesia are dissolved in nitric acid (not in excess), a small excess of magnesia is now added, the whole boiled, filtered, and made up to 2 litres. *Ammonium nitrate*, a 10 per cent. solution. *Magnesia mixture*.—22 grams of crystalline magnesium chloride, 280 grams ammonium chloride, and 700 c.c. of 0.96 ammonia are mixed as usual, and made up to 2 litres. *Dilute ammonia* contains 1 part of ammonia (sp. gr. 0.96) to 3 parts of water. *Ammonium molybdate* by Fresenius' methods.

D. A. L.

**Volumetric Estimation of Phosphoric Acid.** By J. BONGARTZ (*Arch. Pharm.* [3], 22, 846—854).—Thompson has shown that phosphoric acid can be estimated volumetrically by means of standard potassium or sodium hydroxide solution, using methyl-orange or phenolphthaleïn as indicator, whether the acid be present in the free state or combined with sodium or potassium. If potassium hydroxide be added to the phosphoric acid solution until the red colour of methyl-orange changes to pale yellow,  $\text{KH}_2\text{PO}_4$  is formed (112 parts  $\text{KHO} = 142$  parts  $\text{P}_2\text{O}_5$ ). If now phenolphthaleïn be added, and the titration be continued until a red colour appears,  $\text{K}_2\text{HPO}_4$  is formed (again 112 parts  $\text{KHO} = 142$  parts  $\text{P}_2\text{O}_5$ ). On adding hydrochloric or sulphuric acid until the red colour of methyl-orange reappears, the titration with potassium hydroxide can be repeated. Further, the titration of phosphoric acid in combination with calcium, magnesium, iron, and aluminium, can be similarly effected. On dissolving dicalcium phosphate in hydrochloric acid, and adding potassium hydroxide until methyl-orange becomes yellow, the solution then contains potassium chloride, calcium chloride, and monocalcium phosphate. Further, addition of potassium hydroxide until phenolphthaleïn is reddened, produces tricalcium phosphate, dicalcium phosphate, and dipotassium phosphate:— $2\text{CaH}_4(\text{PO}_4)_2 + 6\text{KHO} + 2\text{CaCl}_2 = \text{Ca}_3(\text{PO}_4)_2 + 6\text{H}_2\text{O} + \text{CaHPO}_4 + \text{K}_2\text{HPO}_4 + 4\text{KCl}$ . (In the last titration 168 parts  $\text{KHO} = 142$  parts  $\text{P}_2\text{O}_5$ .) After adding hydrochloric acid, the titration can be repeated as before. Numerical results given show the accuracy of the process. In presence of a sufficiency or an excess of calcium chloride, the monocalcium phosphate is converted entirely into tricalcium phosphate during the titration (224 parts  $\text{KHO} = 142$  parts  $\text{P}_2\text{O}_5$ ). As is known, iron and aluminium are precipitated by ammonia in presence of sufficient phosphoric acid, as tribasic phosphates, insoluble in acetic acid. When dissolved in dilute hydrochloric acid the phosphoric acid can be titrated as above. Phosphoric acid is readily estimated in manures by aid of these methods; iron and aluminium in the solution of the manure are precipitated by ammonia, acetic acid in excess is added, and after a few minutes the precipitate is thrown on a filter and washed, then dissolved in dilute hydrochloric acid, and the solution titrated as above. The filtrate containing the remaining phosphoric acid is treated with a few drops of hydrochloric acid, an excess of solution of iron, aluminium, and calcium chlorides is added, and the phosphoric acid is precipitated in the hot solution by means of ammonia. The precipitate is washed with water containing a little potassium hydroxide dis-

solved in dilute hydrochloric acid, diluted, and titrated after the addition of an excess of calcium chloride.

To determine the total phosphoric acid in manures it is necessary to roast the substance, and then to fuse with sodium carbonate and potassium nitrate. Oxidation with potassium chlorate and hydrochloric acid does not destroy the whole of the organic matter, and this interferes with the end-reaction. The standard potassium hydroxide solution must be free from carbonate and alumina. It is best prepared from caustic baryta and potassium sulphate. J. T.

**Phosphoric Acid Soluble in the Soil.** By A. STUTZER (*Chem. Centr.*, 1884, 329).—Although a solution of ammonium citrate may be of use in determining "reduced" phosphate, it is valueless for the estimation of phosphoric acid which becomes soluble in the soil. The author gives the results he has obtained in the analysis of various phosphatic manures, by using a solution of citric acid, as recommended by Tollens. 5 grams of the manure, which has passed through a 1 mm. sieve, are digested, without heating, for one hour, with half a litre of a 1 per cent. citric acid solution. The liquid is then made up to 1 litre with water, filtered, and the phosphoric acid determined in 50 or 100 c.c. of the filtrate by means of ammonium molybdate. It is not necessary to destroy the citric acid first. In the case of precipitates obtained from iron slag, it is necessary to separate the silica by evaporating 200 c.c. of the citric acid solution to dryness with hydrochloric acid and potassium chlorate, heating the residue to 110°, then taking up with a little nitric acid, and, after diluting to 200 c.c., determining the phosphoric acid in 50 c.c. of the solution. The value of various manures, as determined by analysis, was found to compare well with the trials by actual experiment in the field. P. F. F.

**Estimation of Arsenic in Judicial Cases.** By H. BECKURTS (*Arch. Pharm.* [3], 22, 653—666).—The author reviews the various methods proposed, and gives a new method founded on numerous experiments made by Pehnt and himself. The substance to be examined is reduced to small pieces when necessary, and mixed to a thin paste with 20—25 per cent. hydrochloric acid, and about 20 grams of a 4 per cent. solution of ferrous chloride. The mass is then distilled at the rate of about 3 c.c. per minute, until about one-third has passed over. Substances containing much water are previously evaporated with sodium carbonate; or a more concentrated hydrochloric acid may be used. If not too much arsenic be present, all goes over in the first distillate; otherwise 100 c.c. more hydrochloric acid are added, and the distillation is repeated. The presence of ferrous chloride reduces the volatility of mercury, antimony, and tin to a minimum. The distillate, after dilution with water, can be examined directly in Marsh's apparatus. Quantitatively the arsenic can be precipitated as sulphide, or as the magnesium salt, after oxidation and removal of excess of acid by evaporation, or finally volumetrically after neutralisation with alkaline carbonate. By this method the whole of the arsenic from arsenic and arsenious acids passes over. The sulphide is largely decomposed by a first distillation, and a second distillation

increases the amount of arsenic carried over. Of metallic arsenic, the oxidised portion goes over entirely; of the unoxidised portion a little only passes over.  
J. T.

**Hydrochloric Acid in Marsh's Apparatus.** By H. BECKURTS (*Arch. Pharm.* [3], 22, 681—684).—Objections have been made by various writers to the employment of hydrochloric acid in Marsh's apparatus.

The author experimented with 10 per cent. and 15 per cent. hydrochloric acid, and with 19 per cent. sulphuric acid. Drying tubes charged with calcium chloride, with and without stick potash, were used. He found that the mirror appeared in much less time with the 15 per cent. hydrochloric acid than with the sulphuric acid; also that the employment of the potash is unnecessary.  
J. T.

**Preparation of Hydrochloric Acid free from Arsenic.** By H. BECKURTS (*Arch. Pharm.* [3], 22, 684—685).—Arsenic can be perfectly removed from hydrochloric acid by fractional distillation with the addition of ferrous chloride. The more concentrated the acid, the more readily does the arsenic distil over in the first portions. When acid of 30—40 per cent. strength is distilled, the first 30 per cent. contains the whole of the arsenic, the next 60 per cent. portion is free from arsenic; a 20—30 per cent. acid, free from arsenic, is thus obtained.  
J. T.

**Action of Boric Acid on some Colouring Matters.** By A. JOLY (*Compt. rend.*, 100, 103—105).—Helianthin, tropeolin OO, and Porrier's orange No. 3, are not affected by boric acid in dilute or concentrated, hot or cold, solutions. Further, when a solution of borax is mixed with hydrochloric, sulphuric, or nitric acid, one equivalent of boric acid is liberated for each equivalent of the stronger acid, and it follows that a solution of borax may be accurately titrated by means of any of these acids if one of the colouring matters mentioned above be used as the indicator. Conversely, a standard solution of borax can be used for titrating acid liquids, the only disadvantage being that borax is comparatively slightly soluble in water. The solution, however, does not attack glass, and retains its strength for any length of time, and the end-reaction is very sharply defined.

The basic constituent in a borate of an alkaline earth can be estimated by decomposing the borate with excess of standard hydrochloric acid, adding a few drops of the indicator, and titrating with ammonia until the colour of the liquid changes to pale-yellow.

Phenolphthalein cannot be used in the titration of solutions of boric acid, since the colour change is continuous and not sudden.

C. H. B.

*Note by Abstractor.*—These results agree with those obtained by Thomson (*Abstr.*, 1883, 825).

**Estimation of Potassium in Manures.** Method adopted for 1885, by the Association of Official Agricultural Chemists. (*Chem. News*, 51, 29.)—10 grams of the manure are boiled with 5 c.c.

of strong hydrochloric acid and 300—400 c.c. of water for 10 minutes; the solution is cooled, made up to 1 litre, and filtered through a dry filter. 50—100 c.c. of the filtrate are taken for analysis, and after the removal of sulphuric acid by means of barium chloride and hydroxide of barium by ammonium carbonate, and of ammonium salts and much organic matter by gentle ignition, the mixed chlorides are dissolved in water, treated with sufficient platinic chloride to combine with both sodium and potassium salts, and evaporated almost to dryness. The cold mass is then treated with alcohol, filtered, washed with alcohol, dried at 100° and weighed. D. A. L.

#### **A New Reaction of Sodium, Ammonium, and Lithium Salts.**

By H. HAGER (*Chem. Centr.*, 1884, 651).—The reagent is prepared from 5 parts of crystallised tin chloride, 10 parts distilled water, and as much of a solution of potassium hydroxide of sp. gr. 1.145 as will produce a nearly (but not completely) clear solution. After an hour's standing, there is added 5 more parts of potassium hydroxide solution and 15 parts of water, and the liquid after the lapse of several hours is filtered. On adding this liquid to a solution containing the smallest trace of any sodium salt, a white cloudiness or precipitate shows itself. When the quantity of the sodium salt is extremely small, a few minutes are required for the reaction. Lithium and ammonium salts behave like sodium salts. R. R.

#### **Determination of Silver and Copper in the same Solution.**

By J. QUÉSSAUD (*J. Pharm.* [5], 10, 260—262).—A standard solution of potassium ferrocyanide added to a faintly acid or neutral solution containing silver and copper, precipitates the silver first, and the amount of standard solution required to produce a persistent red tinge in the white precipitate of silver ferrocyanide indicates the amount of silver present. A slight excess of ferrocyanide is then added to precipitate all the copper, when, by adding a standard solution of Rochelle salt in an alkali, the red copper ferrocyanide is destroyed, and the amount of alkaline solution required indicates the amount of copper present. H. B.

#### **Volumetric Determination of Alumina in Lime and Cement.**

By H. PRUNIER (*J. Pharm.* [5], 10, 97—100).—The process depends on the use of a solution 1 : 5000 of tropeolin OO as indicator, for, unlike litmus, it is not affected by the neutral salts of aluminium. A known weight of cement is dissolved in moderately strong nitric acid, and the solution diluted and coloured with some 10 drops of the tropeolin solution; ammonia is then added to exact neutralisation of the free acid, that is, until the red colour has changed to a pale yellow. The alumina is then precipitated by a known volume of seminormal ammonia solution, the whole made up to a given bulk and filtered. The excess of ammonia employed is determined by a decinormal nitric acid, litmus being used as indicator.

If iron is present, it is determined by titration with potassium permanganate and allowed for. Very satisfactory test analyses are given. H. B.

**The Volumetric Determination of Manganese.** By SCHLAGDEN-HAUFFEN (*J. Pharm.* [5], 10, 337—342).—The precautions to be taken in using Leclerc's method are investigated. The manganous salt (sulphate) is heated with an excess of lead dioxide in presence of nitric acid; the solution must be moderately concentrated, not containing less than 0.1 per cent. of manganese; the nitric acid must constitute at least 2 per cent. of the boiling solution, but it may be much larger. The permanganate formed is at once titrated with a solution of mercurous nitrate until the pink colour is destroyed; if the solution do not contain sufficient acid, a brown precipitate, probably a manganite of mercury, will be formed. H. B.

**Electrolytic Estimations.** By J. WIELAND (*Ber.*, 17, 2931—2935).—In reply to Classen's answer (this vol., p. 190) to his former criticism (*Abstr.*, 1884, 1426), the author states that in his experiments he did take all the precautions and follow all the directions given in Classen's earlier papers. He further points out that if Classen's results are expressed in percentages instead of in absolute weight (as given in Classen's paper), they will be seen to be far from satisfactory, varying in some cases as much as 1.7 per cent. from one another and from theory. He therefore insists that, especially in the separation of manganese and iron, Classen's methods are not practically available. L. T. T.

**Examination of Water for Organisms.** By H. S. CARPENTER and W. O. NICHOLSON (*Analyst*, 9, 94—96).—If a sample of water contains but few organisms, these may easily escape observation under the microscope; the authors have, therefore, devised a method by which these organisms may be cultivated, and consequently become so numerous as to be readily recognisable. The necessary apparatus consists of:—1. A short-necked four-ounce flask, fitted with a caoutchouc stopper through which two tubes pass; they are bent at right angles, and have their external ends drawn out. 2. A tube with a bulb (about 25 c.c. capacity) blown on the side, and the ends tapering to fine points. 3. A long combustion-tube 18 inches long, loosely packed for 10 inches with asbestos, which can be connected with a refrigerator. About 50 c.c. of Pasteur solution are boiled in the flask, the combustion-tube is heated to, and kept at, a red heat, a slow current of air is passed through, the flask is attached, and the tubes are sealed up while the sterilised air is passing and the solution is boiling. A bulb-tube is sealed up at one end, distilled water is introduced and boiled off, and the other end is sealed up while the tube is full of aqueous vapour; one end is now broken off under the surface of the water to be examined, and when the bulb is full the end is immediately sealed up again. The heated combustion-tube is now connected with the refrigerator, a rapid current of air is passed to clear the apparatus; one end of the bulb-tube is connected by means of india-rubber tubing with the refrigerator which is now cooled, the other by a similar connection with one of the flask-tubes; all the ends are broken by pressing the india-rubber connections, and the water from the bulb-tube rushes into the partially vacuous flask followed by the cooled sterilised air, the flask-tube is then sealed up and placed in a convenient



place for the development of the organisms, and the apparatus disconnected. All requisite precautions are taken to avoid the admission of extraneous organisms. D. A. L.

**A Uniform Method for the Analysis of Wines.** (*Chem. Centr.*, 1884, 652—656.)—The Report of the Commission appointed by the Imperial Board of Health. It contains:—1. Instructions for the collection and transmission of samples. 2. The analytical methods for the estimation of the natural constituents, and for the detection of adulterations. 3. Data for judging wines. R. R.

**Examination of Glycerol.** By H. ENDEMANN (*Chem. Centr.*, 1884, 454).—On testing glycerol for grape-sugar by boiling it with an alkaline copper solution, a precipitate of cuprous oxide was obtained, but only after long standing. Experiments were, therefore, made with the view to ascertain whether glycerol prevented or retarded the oxidation of grape-sugar by the copper solution. It is found that no such action takes place, so that the above observation must be due to the reduction of the cupric solution by the glycerol itself. In estimating sugar, the glycerol should be diluted, and the slow precipitation due to the glycerol neglected. A. K. M.

**Estimation of Saccharose, Glucose, and Lactose.** By BIGNAMINI (*Chem. Centr.*, 1884, 499).—The method described for estimating the above substances in condensed milk is as follows:—The amount of glucose or invert-sugar and of lactose, which is necessary for the precipitation of 1 gram of cuprous oxide, is first ascertained; this is calculated thus:—

$$\begin{array}{rclcl} \text{Gram.} & \text{Gram.} & \text{Gram.} & & \text{Gram.} \\ 0.0993 : 0.050 & = & 1 : \beta\beta & = & 0.5035, \text{ and} \\ 0.0993 : 0.067 & = & 1 : \text{LL} & = & 0.6747. \end{array}$$

An aqueous extract is prepared from a certain weight of the condensed milk, and an aliquot part of the measured liquid is treated on a water-bath with an excess of Fehling's solution. The weight of the precipitated cuprous oxide is called  $r$ , and is due to the milk-sugar and invert-sugar. The filtrate and washings are freed from copper, boiled with dilute mineral acid in order to invert the saccharose, and again treated with Fehling's solution; the weight of the precipitate when multiplied by 0.95 gives the amount of saccharose present. A fresh portion of the original solution is taken, the saccharose and lactose inverted, and the total invert-sugar estimated. On subtracting from this the amount of cane-sugar already found, the residue is the sum of the inverted milk-sugar together with the original dextrose; this is called  $g$ . From the data obtained, the amounts of milk-sugar and dextrose can be calculated: the inverted milk-sugar and the original invert-sugar being represented by  $x$  and  $y$ ,  $x + y = g$ —

$$x = \frac{\beta Lr - Lg}{0.95\beta - L}; \quad y = \frac{\beta Lr - 0.95\beta g}{0.95\beta - L} \quad \text{A. K. M.}$$

**Action of Lead Acetate on Glucose and Lactose.** By M. RUBNER (*Zeit. f. Biol.*, **20**, 397—413).—When lead acetate and ammonia are added to a dilute solution of glucose until a permanent precipitate is caused, and the solution either boiled for 20—25 seconds, or allowed to stand at the temperature of the room for some time, a red colour is produced. The reaction is much more delicate if the lead acetate is added first, and the solution then boiled before the addition of ammonia. The precipitate first formed dissolves on heating, but reappears on cooling. In a solution containing glucose only, 0.025 per cent. can be readily detected, but the delicacy of the reaction is greatly diminished in presence of other substances (dextrin for instance; in this case, less than 0.12 gives an unsatisfactory reaction).

A solution of lactose treated in a similar way gives scarcely any reaction if boiled for 25 seconds; but, on the other hand, if the boiling is prolonged for 2 or 3 minutes a fine red colour is produced. Consequently, there is little fear of confusion, as 25 seconds is always sufficient to produce the glucose reaction. Moreover, there are certain other distinctive features in the lactose reaction: the solution first becomes yellow, soon passes to red, whilst the precipitate darkens and finally settles down as a brick or copper coloured powder, leaving the supernatant fluid colourless; at the same time small hard red-coloured crystals are found on the walls of the glass vessel.

The author has determined also the delicacy of these reactions as applied to urine; if the sp. gr. is more than 1010, the urine should be diluted with its own volume of water. Instead of filtering off the first precipitate with lead acetate and then adding a sufficiency, it is preferable to precipitate the urine cautiously with ferric acetate, and then proceed in the usual way. The lactose reaction is more delicate in urine than in a watery solution. The addition of lead acetate and ammonia must be varied according to the quantity of glucose or lactose present; 3 grams of lead acetate is usually sufficient for 10 c.c. of urine.

J. P. L.

**Analysis of Honey.** By W. BISHOP (*J. Pharm.* [5], **10**, 459—461).—But few analyses of honey have been published. The author has found in genuine samples from 0 to 16.1 per cent. of crystallisable sugar, and 62.6—79.4 per cent. of sugars capable of reducing Fehling's solution, the total amount of sugars varying from 71—80 per cent. The optical rotation before and after inversion bears no relation to these numbers.

H. B.

**Analysis of Honey.** By O. HEHNER (*Analyst*, **9**, 64—68).—The author has examined 25 samples of genuine honey, mostly of known origin. The composition of honey does not seem to be affected by the blossoms from which it is obtained. The fluidity or solidity of honey does not depend on the amount of moisture. In these experiments, determinations were made of moisture, loss at 100°, of glucose by Fehling's solution before and after inversion, of rotatory power before and after fermentation, and of solid matter remaining after the fermentation with yeast, of a 10 per cent. solution. The composition of various

samples of honey differed to some extent amongst themselves. The following are the maximum, minimum, and mean values per cent. :—

	Maximum.	Minimum.	Mean.
Moisture . . . . .	23·26	12·43	19·3
Glucose . . . . .	75·34	61·42	67·2
Other constituents	16·51	8·48	13·5

In eight cases, the amount of glucose after inversion was practically the same as the amount before inversion. In seven cases, it was somewhat greater, in one case only reaching +2·49 per cent. ; in ten cases it was slightly lower, reaching -5·23 per cent. in one instance only (comp. Abstr., 1882, 1327). The rotatory power both before and after fermentation was in most cases 0, and, with one exception, did not in any case exceed + or -2 divisions of a Soleil-Ventzke polariscope. After fermentation, there is either no glucose at all, or only a very small quantity, whilst the total solids (less glucose) in one case only exceeded 4·77 per cent. ; there is therefore no unfermentable saccharine matter in honey. Alcohol simply produced a faint turbidity in all the samples ; barium chloride gave a similar result. The sp. gr. in all samples experimented with gave a number too high for the glucose alone, and too low for the glucose and other constituents. The author concludes that the moisture in genuine honey does not exceed 23 per cent. ; the amount of glucose is about the same after as before inversion ; the non-saccharine solid matter after fermentation (as above described) does not exceed 5 per cent. ; whilst the rotatory power is 0 or thereabouts (lævorotation indicates crystallisation in the comb, dextrorotation presence of starch-sugar, &c.). These results agree with previous investigations as to the amount of sugar in honey (Abstr., 1878, 969 ; 1881, 316).

D. A. L.

**Determination of Starch in Gluten-bread.** By A. MALLAT (*J. Pharm.* [5], 10, 114—116).—In a previous paper, the author made use of a well-known process, namely, the conversion of the starch into glucose by heating it with sulphuric acid and steam, and subsequent titration with Fehling's solution. Richard has recently criticised this method unfavourably, and proposed the following :—The material is kneaded under water in a small bag until all starch is removed ; the wash waters are concentrated, and then heated in a sealed tube with sulphuric acid at 105° ; the glucose is finally determined. The author, however, finds this method to be practically worthless, as 15 hours' kneading and 70 litres of water are required for a few grams of material.

H. B.

**Test for the Presence of Tartaric Acid in Citric Acid.** By T. PUSCH (*Chem. Centr.*, 1884, 497).—A gram of citric acid and 10 grams of pure concentrated sulphuric acid are introduced into a dry test-tube, which is then surrounded with water kept nearly at its boiling point for an hour. If the citric acid be pure, a lemon-yellow solution will be obtained, but if it contain only half a per cent. of tartaric acid a brownish coloration will develop after 25—30 minutes, becoming reddish-brown after an hour.

A. K. M.

**Free Acid in Oils.** By L. ARCHBUTT (*Analyst*, 9, 170—171).—For the titration of free acid in oils, normal soda is recommended, and the oils are prepared for titration in the following manner:—Redistilled methylated spirit is neutralised with normal soda, using phenolphthaleïn as indicator. For the determination of oleic acid, 50 grams of oil are mixed with 100 c.c. of the neutralised spirit and a few drops of phenolphthaleïn; whilst, for the determination of palmitic or stearic acid, 10 grams of oil or fat, 20 c.c. of the spirit, and a few drops of the same indicator are taken. Solid fats are kept fused during titration by occasional warming. For free mineral acids, the solution is prepared by agitating with water and adding methyl-orange, an indicator not affected by fatty acids. D. A. L.

**Rape Oil, Beef Fat, and Mutton Dripping.** By C. T. KINGZETT (*Analyst*, 9, 15—18).—50 grams of a sample of rape oil of sp. gr. 0.915 yielded, after saponification, a quantity of barium salt corresponding with 51.2 grams of brassic acid. A sample of beef fat free from tissue when similarly treated yielded 26.33 per cent. of oleic acid and 71.66 per cent. solid fatty acids, whilst a sample of purified mutton dripping contained 36.55 per cent. of oleic acid. Both the beef and the mutton fat yielded a very small quantity of a volatile acid product; its aqueous solution gave precipitates with solutions of silver, copper, barium, and calcium salts, whilst with strong sulphuric acid and alcohol it gave off an ethereal odour. The author has observed that neither brassic acid from rape oil nor oleic acid from beef or mutton fat, absorbs oxygen during an exposure of one month to atmospheric air. D. A. L.

**Milk Analysis.** By M. DECHAN and T. MABEN (*Analyst*, 9, 186—189).

**Butter Analysis.** By W. FOX and J. A. WANKLYN (*Analyst*, 9, 73—74).—The authors have shown that butter yields ethyl butyrate when heated with alcoholic potash, and on this they have founded the following method of analysis. To 5 grams of the clarified butter, 100 c.c. of alcohol (sp. gr. 0.838) and 0.5 gram solid potassium hydroxide are added; the mixture is distilled to dryness, and the distillate is received in a stoppered bottle containing 40 c.c. normal soda solution. After agitation, the excess of soda is titrated with normal sulphuric acid. Several satisfactory determinations have been made by this method, the distillate from good butter always consuming alkali, whilst that from inferior butter, cocoa-nut-, and various other fats and oils does not. D. A. L.

**Testing Aniline Hydrochloride.** By R. WILLIAMS (*Chem. News*, 50, 299).—The three chief points for investigation are, firstly, the absence or presence of *grit*, which would injure the “doctors;” secondly, the *acidity*, as too much acid injures the fabric; and, thirdly, the purity of the aniline used in the preparation of the hydrochloride. Dissolve the hydrochloride in water, insoluble matter is grit, which,

if considerable, must be washed, dried, and weighed. Acidity is determined by titration with standard soda. The purity of the aniline is tested by decomposing the hydrochloride with soda, extracting with ether, and oxidising the aniline obtained in this manner, by digesting with arsenic acid at  $180^{\circ}$ . The resulting melt should give a colourless solution; a magenta coloration would indicate the formation of rosaniline, and therefore the presence of toluidine. The presence of any ammonium salts would be detected during the heating with soda. The aniline hydrochloride should not leave any ash. The quality of the colour is tested by printing, steaming, &c., and comparing with a standard colour. D. A. L.

**Commercial Phenols.** By C. CASTELAZ (*Bull. Soc. Chim.*, **42**, 574—580).—In this paper, the author gives his general methods for the analysis of English carbolic acids, known as "crude" and "liquid," of various percentages. The crude acid is obtained from the coal-tar distillates by shaking with soda and subsequent treatment with an acid, and contains, besides phenol and its homologues, non-saponifiable oils and naphthalene in solution, together with water and ammonium sulphide. The author subjects this to fractional distillation to get an approximate knowledge of its constituents. The "liquid carbolic" contains chiefly cresols, with very little phenol. The author tests by shaking measured samples in tubes with water dilute sulphuric acid, and caustic soda, and lastly by fractional distillation.

J. K. C.

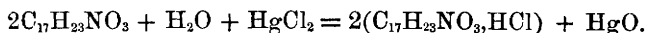
**Detection of Morphia in the Urine.** By NOTTA and G. LUGAN (*J. Pharm.* [5], **10**, 462—463).—In cases of morphiomania, the bulk of this alkaloid taken is eliminated unaltered in the urine, and may be easily detected, since at least 0.1 gram is taken daily. H. B.

**Assay of Cinchona Bark.** By A. PETIT (*Analyst*, **9**, 126—128). The finely powdered bark is exhausted by agitating it for one hour, at intervals of five minutes, with 20 times its weight of a mixture of about 1 part of ammonia, 2 parts of 95 per cent. alcohol, and 23 parts of ether (sp. gr. 0.724). A measured quantity of the ethereal extract is treated with dilute sulphuric acid to remove the alkaloids, which are precipitated from the aqueous solution by means of excess of sodium hydroxide, dried at  $100^{\circ}$ , and weighed for total alkaloids.

To estimate quinine, these dry alkaloids are dissolved in sulphuric acid and agitated with ether and ammonia. The ethereal extract is treated with dilute sulphuric acid and rendered faintly alkaline with ammonia; the sulphate of quinine crystallises out, is filtered off, washed with a cold saturated solution of quinine sulphate, dried at  $100^{\circ}$ , and weighed. The purity of the quinine sulphate may be proved by the polariscope, for which purpose the author advocates the following plan: 1 gram basic sulphate dried at  $100^{\circ}$  is dissolved in 2 c.c. 10 per cent. sulphuric acid, and enough distilled water is added to make up to 20 c.c. The polarimetric deviation for such a solution of pure quinine sulphate is  $-110^{\circ}$  at  $15^{\circ}$  (every  $4^{\circ}$  above  $15^{\circ}$  necessitates the addition of 1 polariscopic degree to the observed figure).

D. A. L.

**Detection of Atropine.** By SCHWEISSINGER (*Arch. Pharm.* [3], 22, 827—828, from *Pharm. Zeit.*).—Gerrard has found (*Arch. Pharm.* [3], 22, 512) that atropine gives a red precipitate with mercuric chloride, whilst most other alkaloids give white ones. Codeine and morphine, however, give pale yellow ones; and strychnine and caffeine give no precipitates. The author has applied this test to several other alkaloids. A 5 per cent. solution of mercuric chloride in 50 per cent. alcohol is employed; 2 c.c. of this is placed on 0.5 to 1 mgrm. of the alkaloid and a gentle heat applied. The reaction with atropine is as follows:—



Arbutin, condurargine, and sparteine give no precipitates; cocaine gives a white precipitate, which only appears in very concentrated solutions, and is soluble on warming; scopolamine gives a yellow precipitate. Hyoscyamine and homatropine give very interesting reactions. Hyoscyamine gives no precipitate if the reagent is added as Gerrard directs, but if only one or two drops of the reagent be added to the alkaloid, a red precipitate appears on gently warming, and is not changed by further addition of the reagent. By these reactions the two isomerides, atropine and hyoscyamine, can be separated. Homatropine gives a yellowish-white precipitate in very concentrated solution only; this disappears on warming, or on addition of more of the reagent. To obtain the reaction, a couple of drops only of the reagent are employed.

These reactions are interesting when compared with Arnold's test for atropine (*Arch. Pharm.*, 1882, 564), namely, the simultaneous action of sulphuric acid and sodium nitrite. Atropine gives a deep yellow colour, which with alcoholic potash becomes reddish-violet and then pale rose. Homatropine gives the same reactions. Gerrard's test is only applicable in the absence of inorganic bodies possessing an alkaline reaction. The method may be employed quantitatively by estimating the amount of mercuric oxide produced. Further, the atropine may be recovered as a double salt by continuing the action of the reagent for some time. The reactions can only be obtained with solutions of the pure alkaloids. A 1 per cent. solution of mercuric chloride gives the reactions even more clearly than the 5 per cent. solution.

J. T.

**Estimation of the Alkaloids in the Root of the *Atropa Belladonna*.** By W. R. DUNSTAN and F. RANSOM (*Pharm. J. Trans.* [3], 14, 623—625).—The method employed for the assay of nux vomica (*Abstr.*, 1883, 689) has now been applied to the determination of the alkaloids in *Atropa belladonna*. 20 grams of the finely-powdered dry root are exhausted by hot percolation with about 60 c.c. of a mixture of equal volumes of chloroform and absolute alcohol. The percolate is agitated twice with 25 c.c. of distilled water; the aqueous layer is then made alkaline with ammonia, and extracted with chloroform. The pure alkaloids are obtained on evaporating the chloroform. As atropine and hyoscyamine are not precipitated by the ordinary reagents for alkaloids, the authors had to test the purity of

the alkaloïd residue in the following manner: it was dissolved in dilute hydrochloric acid, treated with excess of a strong solution of iodine in potassium iodide, the precipitate collected and washed with iodine solution, decomposed on the filter with sodium thiosulphate, and the alkaloïd removed from the solution by agitation with chloroform. By this means, the chloroform residue was found to consist of pure alkaloids. Other experiments show that the alkaloids in question do not appear to undergo any change during the digestion with chloroform and alcohol. The process is recommended as simple and accurate, it requires neither high temperature nor the use of precipitants or acids; moreover, the alkaloids are not heated with alkalis, and the solvent employed extracts a minimum of non-alkaloïd constituents.

D. A. L.

**Microchemical Test for Brucine and Strychnine.** By O. LINDT (*Chem. Centr.*, 1884, 498).—The author has examined the seeds of *Strychnos nux vomica* and *Strychnos ignatii* microchemically for the above alkaloids. Nitric acid and Erdmann's reagent cannot be employed for detecting brucine, as the former gives the xanthoproteic acid reaction, and the latter the sugar-albumin reaction. If, however, the section to be examined is first treated with light petroleum to remove the fat, and a mixture of selenic and nitric acids is afterwards added, the cell-walls assume a bright red colour which gradually changes to orange, and then to yellow, whilst the parts containing no brucine remain uncoloured. In order to detect strychnine, the fat, grape-sugar, and brucine are removed by maceration with light petroleum and with absolute alcohol, and then a solution of cerium sulphate in sulphuric acid is added; this produces a violet-blue coloration in the cell-walls, and afterwards a red coloration inside the cells.

A. K. M.

**Forensic Chemical Detection of Picrotoxin in Animal Liquids and Tissues.** By CHLOPINSKY (*Chem. Centr.*, 1884, 381).—By means of Langley's method as modified by Dragendorff, it is possible to detect 0.1 mgm. of picrotoxin. The latter is moistened with a little strong hydrochloric acid, then dried on the steam-bath, and the residue soaked in very little strong sulphuric acid; on adding an excess of sodium hydroxide, a brick-red coloration is produced. The smallest quantities also reduce Fehling's solution. The author finds that a 0.04 per cent. solution of picrotoxin kills small fishes in two hours, whilst a 0.0004 per cent. takes effect in 48 hours, the symptoms exhibited being very characteristic. The poison may be detected in the vomit, stomach, small intestine, liver, blood, and urine, and the alkaloïd is not destroyed by eight days' putrefaction.

P. F. F.

**Testing for Acetone and Allied Substances in Acetonuria.** By C. LE NOBEL (*Chem. Centr.*, 1884, 626).—The author has found that with an alkaline solution of sodium nitroprusside, so dilute as to have no more than a red tint, a solution of acetone yields a bright ruby-red colour, which in a few moments changes to a straw-yellow. The mixture of either colour, treated with acid, changes on boiling, or on remaining in the air to a greenish-blue tint.  $\frac{1}{4}$  mgm. of acetone

may be detected by this reaction, but with extremely small proportions of acetone, the red colour does not appear, yet the yellow mixture by treatment with acids becomes distinctly violet-coloured.

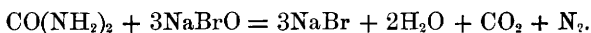
R. R.

**Titration of Urea.** By T. PFEIFFER (*Zeit. f. Biol.*, **20**, 540—565).—The author has made a careful comparison of Liebig's (as modified by Pflüger) and Rautenberg's methods of estimating urea. The essential difference of Rautenberg's method consists in maintaining the urea solution neutral throughout by successive additions of calcium carbonate; under these conditions, the composition of the precipitate differs from that formed when the titration is made according to Pflüger's process, a fact which accounts for the diminished consumption of mercuric nitrate in the former method. The general conclusions from his observations may be summarised as follows:—1st. In estimating the correction for sodium chloride, the amount of free acid should be as small as possible, and 0.1 c.c. should be subtracted from every c.c. of mercuric nitrate used, but in human urine it is preferable to precipitate the chlorine with silver nitrate, as a slight excess of the latter does not influence the result. 2nd. The coefficient for dilution should be determined afresh for every new standard solution.

Observing these precautions, the method has given very accurate results in the author's hands.

J. P. L.

**Estimation of Urea by Bromine.** By H. J. HAMBURGER (*Zeit. f. Biol.*, **20**, 286—304).—The author refers to Pflüger's modification of Liebig's method, which although an improvement leaves much to be desired; his own method is founded on Quinquand's (*Monit. Scien.*, 1882, 2), in which the decomposition of urea by sodium hypobromite is supposed to take place thus:—



This reaction requires the proportion of bromine, sodium hydroxide, and water to be exactly balanced or incorrect results will be obtained; the author claims for his method that it will yield correct results, no matter in what proportions these reagents are present. It consists essentially in adding an excess of an alkaline solution of sodium hypobromite of known strength to the liquid containing urea, then destroying the excess of hypobromite with an excess of standard sodium arsenite (= 19.8 gram  $\text{As}_2\text{O}_3$  per litre), and finally determining the amount of arsenite remaining unoxidised, by titration with standard iodine solution, the amount of urea then being readily calculated from the amount of sodium arsenite remaining unoxidised. The author's experiments as to the accuracy of the method, show that a certain quantity of urea always requires the same amount of hypobromite, and that the dilution of the solution of urea has no effect on the quantity of hypobromite employed.

To decide on the applicability of the method to natural urine, great pains were taken, the urea being determined as described, the effect of its dilution with water studied, pure urea added, and the whole estimated, and lastly sodium hypobromite of various degrees of con-



centration employed; the results of the experiments are given very fully and tabulated. On the whole, they are very satisfactory, the differences falling well within the limits of errors of observation and manipulation: the method is therefore considered applicable to the determination of urea in urine.

The remainder of the paper recommends various precautions in carrying out the process and alternative proportions for the solutions. The author goes at length into an examination of the theory of the process. J. F.

**Estimation of Albuminoids in Urine.** By A. OTT (*Chem. Centr.*, 1884, 500).—To determine the amount of albumin and globulin in urine, the specific rotation of the two together is first ascertained and then that of one constituent. The globulin may, for instance, be precipitated by means of magnesium sulphate; but, according to Hofmeister, the albumin is also thrown down when acid phosphate is present. The author has made a series of experiments with a solution of serum-albumin saturated with magnesium sulphate. The neutral solution was filtered, and to portions (5 c.c.) of the filtrate, varying amounts of neutral sodium phosphate and hydrogen potassium phosphate (in  $\frac{1}{4}$  normal solution) were added; the solutions were then again saturated with magnesium sulphate. The experiments show that the whole of the albumin remains in solution only when at least half the phosphoric acid is present as neutral phosphate. On increasing the proportion of acid phosphate, the albumin is partly precipitated and may be completely thrown down if the acid phosphate alone is present. In carrying out the above estimation, the acid urine must therefore be first approximately neutralised.

A. K. M.

**Examination of Urine for Albumose and Peptone.** By C. MÉHU (*J. Pharm.* [5], 10, 108—114).—Tanret has proposed the following test solution for albumin: potassium iodide 3.32 grams, mercuric chloride 1.35 grams, acetic acid 20 c.c., water 64 c.c. It possesses many advantages, but it may cause the precipitation of uric acid and of alkaloids, such as quinine. In certain urines, after removing any albumin precipitable by heating or by nitric acid, the above reagent has produced a distinct precipitate of albumose or peptone, but whether it can be used for the quantitative estimation of peptones remains to be proved, especially as the nature of peptone is so little understood. Thus commercial peptones are very variable; those obtained with pancreatin are not even precipitated by this reagent. On the other hand, precipitates are sometimes given by urines containing neither albumose nor peptone, for example, those containing mucus; and although the reagent is a valuable one, yet conclusions must be drawn with discrimination. H. B.

**Adulteration of Pepper with Olive Residues.** By E. LANDRIN (*J. Pharm.* [5], 10, 194—200).—In a number of determinations of the cellulose in various peppers and in olive residues, by treatment with ten times the weight of sulphuric acid (100 of acid to 91.8 of water) at 40° the numbers obtained varied from 7.4—16.8 and 55.2—56.7 respect-

ively. The different peppers give results similar to, but not quite identical with, those obtained by Rabourdin, who used a very dilute sulphuric acid. Peppers yield from 7·3—11·8 per cent. of soluble matter to alcohol, whilst olive residues yield but little more than 1 per cent.

H. B.

**Chemical Composition and Testing of Cayenne Pepper.** By F. STROHMER (*Chem. Centr.* 1884, 577).—The following are the results obtained by the author in his examination of the composition of the fruit of *Capsicum annuum*:

	Seeds.	Capsules.	Whole fruit.
Water (at 100°) .....	8·12	14·75	11·94
Nitrogenous matter (protein)...	18·31	10·9	13·88
Fat (ether extract) .....	28·54	5·48	15·26
Non-nitrogenous extractives ....	24·33	38·73	32·63
Fibre .....	17·50	23·73	21·09
Ash .....	3·20	6·62	5·20
	<hr/>	<hr/>	<hr/>
	100·00	100·00	100·00
Nitrogen .....	2·93	1·71	2·22

Whilst the microscope supplies the best and simplest means of detecting adulterations of cayenne pepper, the above figures may nevertheless furnish useful data in certain cases.

R. R.

**Simple Method of Examining Yeast.** By O. MEYER (*Bied. Centr.*, 1884, 792).—A small piece of the compressed yeast is placed in a wine glass which is filled with water at 25°. If the yeast is active it will rise to the surface in 1½—2 minutes, if less good it will require 5 minutes before it rises. Bad yeast will not rise at all.

E. W. P.

## Technical Chemistry.

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**Investigation of Petroleum Lamps.** By L. SCHMELCK (*Dingl. polyt. J.*, **255**, 39—43 and 79—85).—The gradual diminution in the capillary attraction of an oil, and consequently the decrease in the illuminating power, depends on the properties of the oil. Thus petroleum being specifically lighter than rape oil, is more readily raised by the wick; this, however, does not always appear to be the case, as Beilstein has shown that Russian petroleum, although heavier than American petroleum, has a greater capillary attraction. The decrease in the luminosity of a flame, apart from the length of wick up which the oil has to travel, depends to some extent on the change in the composition of the oil on burning, as is shown by the following experiments:—

	Snowflake oil. sp. gr.	Diamond oil. sp. gr.	Kaiser oil. sp. gr.	Young's paraffin oil. sp. gr.
Original oil.....	0·7901	0·8005	0·8019	0·8078
After burning 18 per cent. of oil .....	0·7909	—	—	—
After burning 30 per cent. of oil .....	—	0·8005	0·8022	—
After burning 60 per cent. of oil .....	—	—	0·8029	0·8080
After burning 80 per cent. of oil .....	0·7910	0·8007	—	—

The flashing points of the oils and their different fractions were determined by Abel's method, but there appeared to be no perceptible alteration. An important element in the successful working of an oil lamp is the application of a perfectly dry wick. A new wick should always be dried before it is used. To prevent the decrease in the luminosity of a lamp, Ditmar uses two wicks, by one of which the oil is raised from the reservoir to the uppermost part of the burner, whilst a second wick only a few centimetres long, is enclosed in the first and used for burning. The subjoined table gives the results of some experiments on the influence of the length of the glass chimney on the luminosity of a flame :—

Height of chimney.	Force of flame.	Illuminating power.	Consumption of oil per hour, grams.
Reform burner with 27 cm.	100·0	100·0	41·7
Experiment 1 „ 40 „	93·9	80·0	48·0
„ 2 „ 54 „	65·6	57·0	48·0
„ 3 „ 40 „	131·1	82·2	57·0
„ 4 „ 54 „	135·5	81·6	63·0

In experiments 1 and 2, the flame was turned up to the highest point before the glass chimney was fixed, and in trials 3 and 4 this operation was reversed. Experiments 1 and 2 show that the increase in the force of flame obtained by lengthening the glass chimney fails to neutralise the loss in the illuminating power. It is also shown that as the height of chimney increases the consumption of oil becomes greater.

D. B.

**Zinc in Drinking Water.** By F. P. VENABLE (*Chem. News*, 51, 18).—A spring water of the composition given below was conveyed 200 yards through a galvanised iron pipe, and then stored in a zinc-lined tank painted with white-lead. The water became turbid, and acquired a metallic taste; the pipe had been in use one year when the analysis was made. The results are given in grains per gallon :—

	SiO <sub>2</sub> .	CaO.	MgO.	Alkalis.	Cl.	SO <sub>3</sub> .	ZnCO <sub>3</sub> .	Total solids.
Spring water..	2·45	0·23	0·17	0·43	0·35	0·19	—	4·34

The water in the tank contained 4·48 grains ZnCO<sub>3</sub>, and, that in the

pipe 4.29 grains  $\text{ZnCO}_3$  per gallon. A trace of iron was observed, but no lead (comp. Abstr., 1884, 697 and 878). D. A. L.

**Naphthalene as an Insecticide.** By E. FISCHER (*Pharm. J., Trans.* [3], 14, 991—992).—Naphthalene has been successfully applied to vines attacked by phylloxera, the parasite is destroyed, and the plant develops fresh healthy rootlets, which even penetrate the naphthalene. A trench, 15 to 20 cm. deep, is dug round the plant a few inches from the stock, 1 kilo. of the hydrocarbon is put in, and the trench filled up again at once. Other experiments show that naphthalene properly applied will not only arrest the growth of micro-organisms, but also eventually destroy them. D. A. L.

**Phloroglucinol as an Antiseptic.** By J. ANDEER (*Chem. Centr.*, 1884, 340—341).—This trihydroxybenzene exhibits a marked contrast in its physiological properties both to pyrogallol and resorcinol, with which it is so closely related. Thus, whereas pyrogallol is poisonous, and resorcinol coagulates both vegetable and animal albumin, phloroglucinol is not poisonous, and actually prevents albuminous liquids, like blood, from undergoing coagulation. Phloroglucinol is also possessed of no antiseptic properties, and its acid, neutral, alkaline, and alcoholic solutions develop fungoid growths with greater readiness than any other known chemical preparations. P. F. F.

**Recovery of Sulphur from Hydrogen Sulphide by Means of Nitrohydrochloric Acid in Presence of Air.** By G. LUNGE (*Dingl. polyt. J.*, 255, 38).—The author had some experiments made at Weldon's instigation, with the object of ascertaining whether the sulphur could be recovered from sulphuretted hydrogen by the use of nitrohydrochloric acid. Weldon's idea was to separate the sulphur by means of this acid and simultaneously recover the oxidising substances contained in the acid, by passing a current of air through the mixture, the end-reaction being  $\text{H}_2\text{S} + \text{O} = \text{H}_2\text{O} + \text{S}$ , whereby the nitrohydrochloric acid, nitrosyl chloride, &c., would act merely as carriers of oxygen. The reaction was found to be of no practical utility for the following reasons: (1) Owing to the gradual dilution of the acid; (2) in consequence of the conversion of the sulphuretted hydrogen into sulphuric acid and acids soluble in water, from 69 to 71 per cent. of the sulphur being oxidised to sulphuric acid. The temperature ranged between  $15^\circ$  and  $21^\circ$ . At higher temperatures more sulphuric acid and less sulphur were obtained. D. B.

**Methods for obtaining Phosphates.** (*Dingl. polyt. J.*, 255, 35—38.)—Dreyfus proposes to prepare phosphoric acid from natural calcium phosphate by treating the latter with sulphuric acid. If large quantities of ferric oxide or alumina are present, the success of the reaction is retarded, inasmuch as the residues from the presses become slimy, and hinder the filtering and pressing operations. The phosphate employed at Apt in the department of Vaucluse has the following composition:—

H <sub>2</sub> O.	MgCO <sub>3</sub> .	CaCO <sub>3</sub> .	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .	CaO.	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .	Insoluble.
0·75	1·82	0·68	42·00	4·15	3·60	47·00

The strength of the sulphuric acid used is reduced to 14° B. The phosphoric acid formed is concentrated in leaden pans, heated by a furnace in which the flame does not touch the bottom of the pan, but is made to pass over the surface of the solution to be concentrated. The acid enters the pans at 15° B., and is run off at 45—50°. The furnace is 5—6 m. long, and 1—5 m. in width, and is capable of evaporating 8,000 kilos. phosphoric acid in 24 hours. The pressed residues contain gypsum, the gangue of the mineral, unattacked ferric oxide and alumina, and 40 per cent. of moisture. They are dried, ground, and sold as manure at 9*d.* to 1*s.* 6*d.* per 100 kilos., the percentage of phosphoric acid ranging between 2 and 3. The phosphoric acid is mixed with ground phosphate, and brought into commerce as superphosphate containing 43—44 per cent. of soluble phosphoric acid.

According to Adair and Tomlinson, phosphatic slags or minerals are reduced to powder and roasted if necessary. If the material to be treated consists of tap or mill cinders or compounds of iron and phosphorus, it is heated with a solution of caustic soda in the proportion of 3 equivalent parts of soda for 1 equivalent part of phosphoric acid present. If, however, basic or other slags produced in the manufacture of iron and steel are contained in the material to be treated, the caustic alkalis are replaced by their carbonates. The phosphoric acid of the solution of sodium phosphate thus obtained is then precipitated by lime.

D. B.

**Progress made in the Soda Industry.** (*Dingl. polyt. J.*, 255, 168—172.)—The manufacture of soda by the ammonia process is continuing its rapid advance, and would have involved the closing of a number of Leblanc soda works, but for the formation of a combination among Leblanc soda makers to reduce the production in order to influence the market, and especially to raise the price of bleaching-powder. The only circumstance by which the Leblanc process may continue to exist is that by its means bleaching-powder can be produced very cheaply; Weldon, however, in his Presidential Address delivered at the annual meeting of the Society of Chemical Industry held at Newcastle in 1884, showed that the Leblanc process is not likely to continue or remain the only means of obtaining hydrochloric acid owing to recent discoveries of very important processes.

To recover the chlorine, at present wasted as calcium chloride in working the ammonia-soda process, Mond proposes to evaporate the ammonium chloride liquors. Ammonium carbonate distils over and is condensed and the sodium chloride is fished out as it separates. The solid ammonium chloride remaining in the residue is then treated with enough sulphuric acid to form hydrogen ammonium sulphate, hydrochloric acid being liberated. The hydrogen ammonium sulphate is converted into the normal salt by allowing ammonia to act thereon, or it is used, instead of free sulphuric acid, for dissolving phosphates. The manufactory owned by Brunner, Mond, and Co., pro-

duces annually about 50,000 tons of soda, and by using this process about 128,000 tons of ammonium sulphate would be obtained, which is equivalent to one-third more ammonia than the total quantity at present produced in Great Britain, whilst to employ the vast quantity of hydrogen ammonium sulphate to react on calcium phosphate would involve the annual manufacture of 350,000 tons of manure. These considerations prove the impossibility of applying this process on any extensive scale.

Another idea to obtain hydrochloric acid in connection with the ammonia-soda process, and which Weldon considers has received more attention than it deserves, consists in decomposing salt by sulphuric acid and converting the sulphate thus produced into sodium bicarbonate and ammonium sulphate by treatment with ammonia and carbonic anhydride. It has been ascertained by experiment that the decomposition of sodium sulphate by means of ammonia and carbonic anhydride can be effected without difficulty. Owing to the slight solubility of sodium sulphate at the ordinary temperature, a temperature of  $34^{\circ}$  is employed for the saturation.

Since the essential point which makes the Leblanc process so costly is the preparation of sulphuric acid and sodium sulphate, the decomposition of the latter by ammonia and carbonic anhydride would have no advantage. It has, however, been found by Carey, Gaskell, and Hurter, that on heating ammonium sulphate with sodium sulphate the whole of the ammonia is disengaged and hydrogen sodium sulphate is produced. By the action of salt on the latter sodium sulphate is again obtained, so that theoretically there should be no loss of sulphuric acid. The following are the operations which it is necessary to perform in addition to those of the ammonia-soda process:—(1.) Evaporating to dryness the liquors containing sodium and ammonium sulphates; (2) heating the residue after addition of sodium sulphate; and (3) decomposing fresh portions of salt by hydrogen sodium sulphate.

The quantity of water to be evaporated in the first operation is estimated at  $5\frac{1}{2}$  tons per ton of soda, which would require about 1 ton of coal. For the third operation, half a ton of coal should be sufficient; so that the cost of both operations for labour and fuel could scarcely exceed 11s. or 12s. The value of hydrochloric acid obtained for every ton of Leblanc soda is estimated by Weldon at 48s., and it is thought that the balance of 36s. will more than pay for the second operation.

Weldon would have anticipated an important future for this process were it not for the results of a renewed and successful attempt to obtain ammonia from ammonium chloride by decomposition with magnesia. After experimenting for many years on the decomposition of metallic chlorides, he obtained successful results in 1881 by mixing the chlorides with metallic oxides and exposing the mixture to the action of heat and air. Since 1882 Pechiney and Company of Salindres have been engaged in endeavouring to realise the working of this method, especially as applied to the chlorides of magnesium and manganese. Experiments made on a large scale at Salindres leave no doubt that fully half the chlorine of magnesium chloride may

be obtained directly as free chlorine, by converting the magnesium chloride into magnesium oxychloride and heating the latter in presence of air. The ammonia-soda maker, in order to obtain chlorine from ammonium chloride, would therefore have to evaporate about 5.5 tons of water per ton of soda and heat a mixture of 940 kilos. magnesium chloride with about 400 kilos. magnesia in the presence of air, to obtain a quantity of chlorine corresponding nearly with 1 ton of bleaching-powder and a quantity of hydrochloric acid corresponding with something over 1 ton of hydrochloric acid of 27 per cent.

In discussing the improved processes for preparing chlorine from hydrochloric acid, Weldon refers to a new method which is being worked out at Salindres, by means of which the whole of the chlorine of the hydrochloric acid treated is obtained in a free state. The operation consists in treating manganese peroxide with hydrochloric acid so as to obtain free chlorine and a solution of manganese chloride. The latter is evaporated to dryness and heated in contact with air. The chlorine of the manganese chloride is driven off as chlorine diluted by other gases, and in the residue manganese peroxide is recovered. The process yields the same quantity of strong chlorine gas as can be obtained by the old Weldon process, together with twice the quantity of chlorine diluted by other gases. The chlorine for 1 ton bleaching-powder made by the old process costs about 119s., whilst the new process gives 1 ton of bleaching-powder from less than 1.5 tons of hydrochloric acid of 27 per cent. The value of this quantity of acid being taken at 30s., there remains  $119 - 30 = 89$ s. out of which to pay the cost of evaporating a solution of manganese chloride containing about 1.75 tons water, and heating a mixture of 0.75 ton manganese chloride with a certain proportion of manganese dioxide in the presence of air.

Referring to the numerous attempts made to recover the sulphur from soda-waste, Weldon states that now that the Leblanc process is threatened to be extinguished, a process for recovering both the sulphur and the lime has been discovered. The calcium sulphide contained in soda-waste is brought into solution as calcium sulphhydrate by treatment with sulphuretted hydrogen and water. This solution is boiled, when pure sulphuretted hydrogen is evolved and calcium hydroxide precipitated, thus:  $\text{CaH}_2\text{S}_2 + 2\text{H}_2\text{O} = \text{CaO}_2\text{H}_2 + 2\text{H}_2\text{S}$ . The sulphuretted hydrogen is then burnt with the requisite proportion of air to liberate its sulphur. This operation has been the subject of experiment in the works of Chance Brothers. The apparatus was that patented by Claus of London. It consists of a kiln filled with porous material in which the combustion of the mixture of air and sulphuretted hydrogen is effected. The recovery of the calcium sulphhydrate by treating soda-waste by the above-described method, is in operation at Rassuen, in the South of France, in connection with Lombard's process, in which calcium sulphhydrate is employed to precipitate hydrogen calcium phosphate from the solution obtained by dissolving calcium phosphate in hydrochloric acid. Weldon is of opinion that if the crystalline calcium hydroxide has the same equivalent value as lime, and the conversion of sulphuretted hydrogen



into sulphur is practically complete, then the problem of utilising alkali-waste will have been solved satisfactorily. D. B.

**Celestine.** By W. MOODY (*Dingl. polyt. J.*, 255, 87).—Having obtained strontium sulphide by heating celestine in admixture with coal, the author proposes to mix the sulphide whilst hot with water to form a thin pasty mass which is then mixed with a quantity of soda or potash sufficient to combine with the sulphur of the sulphide. On cooling, strontium hydroxide crystallises out. The mother-liquor may either be concentrated until hydrated sulphide separates from it, or it may be treated by sulphurous acid for the conversion of its sulphide into thiosulphate with precipitation of free sulphur.

D. B.

**Density of Solutions of Pure and Commercial Aluminium Sulphate, and Solubility of Alum in Aluminium Sulphate.** By C. REUSS (*Ber.*, 17, 2888—2892).—A great deal of the alum and aluminium sulphate of commerce is now obtained by the treatment of bauxite and alunite with sulphuric acid. Solutions are thus obtained which consist, when bauxite is used, of nearly pure aluminium sulphate, and when alunite is employed, of a concentrated solution of

Per cent.	Pure aluminium sulphate.				Commercial aluminium sulphate.
	$d_{4^{\circ}}^{15^{\circ}}$	$d_{4^{\circ}}^{25^{\circ}}$	$d_{4^{\circ}}^{35^{\circ}}$	$d_{4^{\circ}}^{45^{\circ}}$	$d_{4^{\circ}}^{15^{\circ}}$
1.....	1·017	—	—	—	1·0069
2.....	1·027	—	—	—	1·0141
3.....	1·037	—	—	—	1·0221
4.....	1·047	—	—	—	1·0299
5.....	1·0569	1·0503	1·045	1·0356	1·0377
6.....	1·0670	—	—	—	1·0416
7.....	1·0768	—	—	—	1·0481
8.....	1·0870	—	—	—	1·0592
9.....	1·0968	—	—	—	1·0650
10.....	1·1071	1·1022	1·096	1·085	1·0730
11.....	1·1171	—	—	—	1·0794
12.....	1·1270	—	—	—	1·0860
13.....	1·1369	—	—	—	1·0960
14.....	1·1467	—	—	—	1·1059
15.....	1·1574	1·1522	1·146	1·1346	1·1097
16.....	1·1668	—	—	—	1·1169
17.....	1·1770	—	—	—	1·1199
18.....	1·1876	—	—	—	1·1269
19.....	1·1971	—	—	—	1·1339
20.....	1·2074	1·2004	1·192	1·1801	1·1440
21.....	1·2168	—	—	—	1·1488
22.....	1·2274	—	—	—	1·1589
23.....	1·2375	—	—	—	1·1628
24.....	1·2473	—	—	—	1·1689
25.....	1·2572	1·2483	1·2407	1·2295	1·1798

alum containing excess of aluminium sulphate. With the object of placing a ready means of estimating the strength of such solutions in the hands of manufacturers, the author has made a careful series of determinations of the densities of solutions (i) of pure, and (ii) of average commercial aluminium sulphate. The composition of the sample of commercial aluminium sulphate used was  $\text{Al}_2\text{O}_3 = 13.52$  per cent.,  $\text{SO}_3 = 31.58$  per cent.,  $\text{Fe} = 0.33$  per cent.,  $\text{K}_2\text{O} = 0.93$  per cent.,  $\text{H}_2\text{O} = 52.27$  per cent. The pure salt contained 40.27 per cent.  $\text{H}_2\text{O}$ .

The densities are compared with water at  $4^\circ$ , and the results are given in the table (p. 458).

The author has investigated the solubility of alum in solutions of aluminium sulphate. He finds that the addition of 1 per cent. of potassium sulphate to solutions of aluminium sulphate of a strength of 7 per cent. and upwards, causes a deposition of alum, but no precipitation takes place in solutions of 6 per cent. and below. It is therefore advisable for the alum manufacturer to employ his aluminium sulphate solutions of a greater strength than 7 per cent.

L. T. T.

**Action of Dilute Acids on Bottle Glass.** By E. EGGER (*Dingl. polyt. J.*, 255, 127).—The author has investigated the action of dilute tartaric, hydrochloric, and sulphuric acids on different bottles, and found, in some cases, a considerable decrease in the acidity of the glass. An examination of the glass of two bad bottles (I and II), two bottles of medium quality (IV and V), and two good bottles (III and VI), gave the following results:—

Experiment.	$\text{SiO}_2$ .	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ .	Mn.	CaO.	MgO.	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .
I .....	53.15	13.14	Traces.	14.69	0.84	14.83	3.21
II .....	52.90	12.85		15.88	0.95	14.27	3.16
III .....	56.34	11.34		16.05	1.15	11.44	3.46
IV .....	55.02	12.11		16.21	1.04	12.11	3.59
V .....	62.95	6.80		16.72	1.80	9.26	1.40
VI .....	57.16	11.79		11.79	0.90	15.41	2.72

It will be seen that the quantity of silicic acid present is not sufficient for the production of a compound capable of resisting the action of acid solutions.

D. B.

**Gilding Earthenware Goods.** (*Dingl. polyt. J.*, 255, 126.)—To decorate objects of porcelain or stoneware, the Ilmenau Porcelain Works recommend that the materials should be strongly heated, the places to be set off coated with a paste composed of gum and pottery material (slip), and dusted with powdered porcelain. They are then to be dried and burnt in glaze-kilns. After cooling, the raised places are coated with gold or silver leaf or a metallic colour, and heated in a muffle furnace. In the finished articles, the decorated places come out in a bright form or in biscuit.

D. B.

**Japanese Materials for the Manufacture of Ultramarine.**

By K. IWABUCHI (*Chem. News*, 51, 5—7).—The author has tried to prepare ultramarine from various Japanese clays, of which the following alone gave blues; they had the composition:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.
1. Goto kaolin...	48·65	36·99	0·48	0·43	0·13	6·62
2. Gairome.....	53·90	41·95	1·25	0·56	—	1·78
3. Shigaraki ....	58·42	28·37	1·20	1·42	—	2·53
4. Shiraye .....	47·74	36·68	0·42	0·99	0·11	0·24

	Na <sub>2</sub> O.	Moisture.	Ratio, Al <sub>2</sub> O <sub>3</sub> : SiO <sub>2</sub> .
1. Goto kaolin ....	0·85	6·03	1 : 2·23
2. Gairome.....	0·48	—	1 : 2·20
3. Shigarki.....	2·65	5·29	1 : 3·55
4. Shiraye .....	0·21	13·64	1 : 2·21

The product from 1 is dull, from 2 bad, from 3 reddish, from 4 dark, fine, and with lustre. Using Gentile's proportions with the clay 4, the yield is about a third of the original mixture. The addition of silica to raise the ratio of Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> = 1 : 3, gave only moderately good results, and that only with a low heat of calcination. The sulphate ultramarine from this clay (4) was not good, and after the addition of silica was an utter failure. Various proportions have been tried, using both carbonate and sulphate, but without any improvement on the above result. From this it is evident that a good ultramarine may be produced from a clay in which the ratio of the Al<sub>2</sub>O<sub>3</sub> to the SiO<sub>2</sub> is 1 : 2.

D. A. L.

**Action of Concentrated Sulphuric Acid on Lead and its Alloys.**

By L. PITKIN (*Analyst*, 9, 119—125).—In order to decide as to the advisability of employing pure lead, or an alloy of this metal, for the storage and evaporation of sulphuric acid, the author has made the present experiments; 40 samples of lead and its alloys have been submitted to the action of cold and warm concentrated sulphuric acid. The alloys contained 100 parts of lead, mixed respectively with  $\frac{1}{2}$ , 1, 2, 3, 5, and 10 parts of one of the metals antimony, tin, bismuth, cadmium, silver, and zinc; the alloys were rolled out to about the same thickness. For each experiment 2 sq. in. were exposed to 10 c.c. of acid, in one series for 24 hours at 20°, in another series for 1 hour at 100°, and in each case the loss in weight of the metal was ascertained. With pure lead, the results agree with those obtained by Napier (*Chem. News*, Dec., 1880). With alloys, the action of the cold acid on the lead is diminished by the admixture of antimony in any of the above proportions and by bismuth, cadmium, or silver, if below 5 per cent., whilst it is increased by the last three metals when they exceed 5 per cent., and by tin or zinc in all the proportions. At 100°,  $\frac{1}{2}$  or 1 per cent. of bismuth, or antimony in any of the proportions mentioned above, greatly increases the solubility of the lead, cadmium or zinc increases it slightly, whilst it is diminished by the presence of tin, silver, or more than 1 per cent. of bismuth.

D. A. L.

**Proportion of Cadmium in Zinc-dust.** (*Chem. Centr.*, 25, 591).—Cadmium being more volatile than zinc, the zinc-dust formed at the beginning of a distillation contains the highest proportion of cadmium. The percentage of cadmium in one case after the first two hours' distillation, was found to be 0.794 per cent., after four hours 0.630 per cent., after six hours 0.283 per cent. R. R.

**Preparation of Zinc Free from Arsenic.** By F. STOLBA (*Chem. Centr.*, 1884, 419).—Zinc free from arsenic and almost free from iron can easily be obtained by subjecting the molten metal of commerce to the simultaneous action of sulphur-vapour and steam. Small spheres, about 5 cm. in diameter, are prepared by mixing plaster of Paris with one-fourth its weight of powdered sulphur, together with the necessary quantity of water. These balls are depressed to the bottom of the crucible containing the molten zinc, and, by giving rise to an abundant evolution of sulphuretted hydrogen and sulphur-vapour, keep the molten metal in violent agitation. The arsenic may be removed by either steam or sulphur-vapour acting alone, but the separation of iron is best accomplished by the combined action of the two. P. F. F.

**Manufacture of Metallic Alloys.** (*Dingl. polyt. J.*, 255, 73—75).—For the preparation of the so-called "Delta metal," Dick and Co. propose to add spiegeleisen or ferromanganese to molten zinc heated at about 900°. In this way, about 9 per cent. of the compound is said to be taken up by the zinc. The saturated compound thus formed is added to molten copper with or without further additions of pure zinc. Silicon, if present, increases the hardness of the alloy; if, however, the ferromanganese or spiegeleisen contains more than 0.5 per cent., a proportionately larger quantity of pure zinc is employed.

Webster manufactures a bronze of bismuth, which is said to resist atmospheric influences, by fusing 1 part of bismuth with 25 parts of nickel, 25 parts of copper, and 50 parts of antimony. A hard alloy is so obtained suitable for the manufacture of reflectors for lamps, also for the preparation of axle-bearings, ventilators, &c. Another hard bismuthic bronze is produced by fusing 1 part of bismuth with 16 parts of tin, and then heating 0.4 part of the alloy thus formed with 45 parts copper, 22.5 zinc, and 32.5 nickel. The bronze alloy is well adapted for the manufacture of screw propellers, tubes, and materials exposed to the action of sea water. Being highly tenacious it may be used for the preparation of telegraph wires, and on account of its sonorous properties is useful for pianoforte wires.

Fleitman has found that nickel, or its alloys with copper, cobalt, and iron, may be fused with zinc, tin, lead, cadmium, iron, manganese, and silver, without destroying the welding property of the compound produced. D. B.

**Preparation of Malleable Ferronickel and Ferrocobalt.** (*Dingl. polyt. J.*, 255, 174).—The *Fonderie de Nickel et métaux*  
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*blancs* in Paris proposes to obtain malleable ferronickel and ferrocobalt either from their ores or by fusing chrome ores with the corresponding quantity of nickel or cobalt. The fusion is conducted in suitable crucibles or furnaces, potassium ferrocyanide and manganese dioxide being added to the mass, and a small amount of aluminium introduced towards the end of the operation. The malleability of the metal thus produced depends on the purity of the ores originally used. When using, for instance, an alloy composed of 70 per cent. nickel and 30 per cent. iron, containing a small percentage of sulphur, 71.9 parts of nickel-melt, 12 parts manganese dioxide, 16 parts potassium ferrocyanide, and 0.1 aluminium, are taken, whilst in the case of ores poor in nickel, containing, for instance, 25 per cent. nickel, 64 per cent. iron, and 11 per cent. of other impurities, a mixture of 82 parts nickel-melt, 8 parts manganese dioxide, and 10 parts potassium ferrocyanide is fused together.

D. B.

### **Toughening (Refining) Gold, Silver, &c., in the Crucible.**

By J. C. BOOTH (*Chem. News*, 51, 16—17).—The author refers to a process for refining gold (Abstr., 1884, 1445), wherein the impurities along with some gold are skimmed off the fused mass, whilst the greater quantity of gold is left practically pure. This process is now applied to silver mixed with foreign metals, such as lead, tin, zinc, antimony, &c. The silver, about 3500 ozs., is fused with 1 oz. or more of anhydrous borax, bone-ash is sprinkled over the surface to about  $\frac{1}{4}$  in. thickness, crystals of sodium nitrate are then dropped in, and the whole mass well stirred and skimmed; the oxidation and skimming being continued until the metal is sufficiently pure. The whole operation lasts but a few minutes. In the case quoted, 50,000 ozs. of commercial silver yielded, by this method, 49,000 ozs. silver tough and pure enough for coinage in less than  $1\frac{1}{2}$  days. The skimmings are fused with charcoal and pearl ash, and when cool the metallic particles are separated from the fused mass by crushing and sifting. The mixture of metals is then gradually heated from below the melting point of lead to a full red heat; runnings from the melted metals being collected at the different temperatures; the first runnings are nearly pure lead. Silver mixed with the other metals mentioned above may be mixed with lead and then treated as described. This process is recommended as a substitute for cupellation, where the latter is not convenient. It can also be employed for the removal of phosphorus from phosphor-bronze, using lime as a covering for the molten metal.

D. A. L.

### **Fusion, Casting, Dephosphorising, and Plating of Iridium.**

By N. W. PERRY (*Chem. News*, 51, 1—5; 19—21; 31—33).—The present communication contains an account of most of the important facts connected with the introduction of iridium into the arts. The greater part has appeared before in this Journal (Abstr., 1882, 703—704; 1884, 400; &c.) and elsewhere, whilst much of it is simply of historical interest. Iron and phospho-iridium unite in all proportions, the alloy is slightly magnetic, but otherwise retains the properties of phospho-iridium as regards incorrosibility and hardness, until

the iron reaches about 50 per cent., when it becomes more and more like iron, but always remains brittle. For casting purposes, the phospho-iridium has to be fused many times until a certain point is reached; each time it is heated it loses phosphorus, therefore the fusion temperature is continually increasing, and if the point is passed more phosphorus has to be added. Iridium plating is now successfully conducted, but as yet the process is secret. Plating from a solution of iridium sodium chloride with a phospho-iridium anode does not answer, because the metal is deposited more quickly than the anode is dissolved, moreover, the coating is too thin and scales off. The applications of iridium have extended greatly, and there are now numerous additions to those already mentioned and suggested (*loc. cit.*). In fact, it can be used for all purposes requiring a metal capable of resisting chemical and mechanical wear, and is apparently unrivalled in this respect. The paper concludes with a bibliography of iridium.

D. A. L.

**On the Influence of Coal Dust in Colliery Explosions.** By W. GALLOWAY (*Proc. Roy. Soc.*, 37, 42—46).

**Recovery of Paraffin and Heavy Oils from Petroleum-residues.** By DURIN (*Chem. Centr.*, 1884, 384).—By distilling petroleum-residues in a vacuum with superheated steam, from 96 to 98 per cent. of paraffin oil can be obtained, whilst ordinary distillation yields only about 50 per cent. These oils, which are gelatinous at ordinary temperatures, contain about 50 per cent. of paraffin, of which 20 per cent. can be recovered. The oils are purified by filtration at 35—40°, and subsequent treatment with 4 to 5 per cent. of sulphuric acid. After subsidence, the oil is separated from the tarry matters by decantation, and then treated with 1—2 per cent. of calcium hydroxide to remove traces of acid. On allowing the mass to slowly cool down to 5°, leafy crystals are obtained, from which the oil is removed by pressure.

P. F. F.

**Preparation of Iodoform, Bromoform, and Chloroform.** (*Dingl. polyt. J.*, 255, 88).—The *Chemische Fabrik auf Actien* in Berlin recommends that iodoform, bromoform, and chloroform should be obtained by electrolytic means from the corresponding halogen derivatives of the alkalis and alkaline earths, in the presence of alcohol, aldehyde, or acetone. For instance, 50 kilos. potassium iodide are dissolved in 300 kilos. water, and the solution is mixed with 30 kilos. alcohol (96 per cent.). The mixture is subjected whilst hot to electrolytic action, a continuous stream of carbonic anhydride being passed into the solution. The iodoform thus obtained is deposited in the form of a crystalline powder.

D. B.

**Presence of Isocyanates in the First Running of the Distillation of Crude Benzene.** By E. NÖLTING (*Dingl. polyt. J.*, 255, 88).—The author has detected the presence of an isonitril (probably methyl or ethyl isocyanate) in light benzene. His researches appear to show that in spite of the small proportion of poisonous ingredients

found in the first distillate from benzene, the working of light benzenes on a large scale may, under certain conditions, produce poisonous effects. He quotes a fatal case which occurred at a factory in Thann (Alsace), where a workman engaged in covering cloth with a solution of caoutchouc in benzene had inhaled the vapour of isonitril, and died from its effects, which are similar to those of prussic acid. To remove this poisonous impurity, light benzenes should be washed repeatedly with sulphuric acid.

D. B.

**Manufacture of Sugar without Bye-products.** By E. REBOUX (*Chem. Centr.*, 1884, 407—408).—The first syrups contain acid potassium and sodium salts of organic acids causing the formation of molasses. These salts are more difficult to remove by osmosis than the mineral salts, viz., chlorides, sulphates, and nitrates. By adding ammonium chloride, double decomposition takes place with formation of chlorides of potassium and sodium, together with organic ammonium salts, and the former diffuse very rapidly, whilst the organic ammonium salts are destroyed in the subsequent treatment with lime. The organic lime salts so formed are then decomposed by carbonic anhydride.

P. F. F.

**New Process of Extraction of Beet.** By BOURY and O. PROVINS (*Bied. Centr.*, 1884, 780—782).—The roots are to be heated to 80°—100° before pressing; thus a juice is obtained clear and pure, and moreover it separates more easily from the mark, and keeps better. A further advantage is that a higher coefficient of purity is obtained than when the juice is expressed before heating; this is demonstrated by comparative experiments on the same sample of roots. By this method less press cake is produced, but its value is raised from say 19·4 to 27·3 francs per 100 kilos., the quantity being reduced from 28 per cent. to 16 per cent., but then this cake is more easily pressed and dried.

E. W. P.

**Butyric Fermentation in the Diffusion Vessels of Sugar Factories.** By P. P. DEHÉRAIN (*Chem. Centr.*, 1884, 403—404).—It has been observed that during the process of diffusion sometimes as much as 1 per cent. of sugar is lost, a considerable quantity of hydrogen being evolved, whilst the juice contains acetic and butyric acids. As the butyric ferment seems to be always present in arable soil, the fermentation is probably induced by the presence of a small quantity of earth which has escaped being washed off the beets. The importance of thoroughly washing the tubers is apparent.

P. F. F.

**Potassio-antimonic Oxalate, a Substitute for Tartar Emetic.** (*Dingl. polyt. J.*, 255, 122—124).—Tartar emetic is being gradually replaced in dyeing and printing by a new antimony preparation having the composition  $C_2O_4SbK_3 + 6H_2O$ , and containing 23·67 per cent.  $Sb_2O_3$ . The commercial product crystallises in white needles resembling oxalic acid or Epsom salt, which are readily soluble in water. It is sold at a moderate price as a substitute for tartar emetic in fixing tannin colours.

D. B.

## General and Physical Chemistry.

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**Coloration of the Hydrogen Flame.** By S. SANTINI (*Gazzetta*, 14, 274—276).—The author, in a former memoir, has shown that by suitably varying the conditions, the flame of hydrogen assumes all the colours of the spectrum. In order to test whether this result was due to impurities contained in the materials from which the hydrogen was evolved, the gas was prepared by heating potassium formate with potash, but the same phenomena were observed. The best method for their production consists in collecting the hydrogen in a bell-jar of 5.6 cm. diameter and 20 cm. length, then holding it with its mouth downwards, applying a light, and gradually inclining the vessel. A tongue of flame is formed, in which all the prismatic colours may be distinguished as the jar is brought into the horizontal position. These phenomena are not peculiar to hydrogen, but may be produced not only with gases, such as carbonic oxide, hydrogen sulphide, and methane, but also with the vapours of combustible liquids, such as the various alcohols, ethereal salts, acetone, benzene, &c. V. H. V.

**Methods of Spectrum Analysis.** By E. DEMARÇAY (*Compt. rend.*, 99, 1069—1071).

**Spectroscopic Studies on Gaseous Explosions.** By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, 36, 471—478).—After briefly recording observations on the spectra of the metals produced by explosions of detonating mixtures in presence of different materials, the authors give a list of the wave-lengths of the iron, copper, nickel, cobalt, lead, silver, chromium, sodium, magnesium, and manganese lines observed. It is noticeable that such volatile metals as mercury, zinc, cadmium, bismuth, and antimony gave no lines. The numerous lines of iron were particularly observed; these were in many cases reversed, thus showing that at the temperature of the explosion the metal was volatilised; and, indeed, Watts has already pointed out that iron is volatile below the fusing point of platinum. It is thus not surprising that iron lines should have been observed accompanying those of hydrogen to great heights in the solar atmosphere, whilst Copeland and Lohse observed in the spectrum of the great comet of 1882, four lines,  $\lambda 5395$ ,  $\lambda 5369$ ,  $\lambda 5326$ , and  $\lambda 5269$ , which are nearly identical with iron lines observed in the flash of the detonating gases. As Gouy has observed, in the spectra of the metals taken in a modified form of a Bunsen's burner, certain iron and other metallic lines not observed in the spectra from detonating gases, the authors question whether this result implies that—when the proportion of air to coal-gas is near the exploding point—the temperature of the inner green cone of a Bunsen burner is higher than that produced by the explosion of hydrogen with oxygen. V. H. V.



**Delicacy of Spectrum Photography.** By W. N. HARTLEY (*Proc. Roy. Soc.*, **36**, 421—422).—In this Abstract, a brief account is given of the length and strength of metallic lines in solutions of definite strength. The sensitiveness of the spectrum reaction in the case of magnesium compounds is practically unlimited, for with a given length of spark  $10^{-8}$  of a milligram could be detected, and the sensitiveness could be increased by increasing the strength of spark. The lines  $\lambda 2801.6$  and  $\lambda 2794.1$  could be detected with a solution containing 1 part of magnesium in  $10^9$  parts of water.

Evidence is also brought forward to show that in the case of the aluminium spectrum, the longest and the strongest lines are not invariably the most persistent; as a general rule, even the longest lines are shortened by great dilution of the solution. From the results obtained, it is proposed to apply, in some few cases, the maps of the spectra for quantitative estimation of the proportion of the metals present.

V. H. V.

**Experiments on Flame.** By G. J. BURCH (*Nature*, **31**, 272—275).—Noticing how even the intense glow of a piece of lime heated to whiteness in the blowpipe flame became invisible in direct sunlight, the author was led to make some experiments to similarly test the sun's light against that of a flame.

When the image of the sun was thrown, by means of a lens, upon the flame of a paraffin candle, a round spot of light of a bluish-white colour, and a peculiar, soft appearance, became visible on the flame itself. To the naked eye, this spot of light was of exactly the same soft quality, and nearly the same colour as the fluorescence produced when sunlight is focussed on to petroleum, or a solution of quinine sulphate. When viewed with the spectroscope, however, this similarity disappeared. The fluorescent solution showed a soft continuous spectrum, whereas the spectrum of the spot of light was much brighter, extended far into the violet, was most intense in the blue, and showed all the Fraunhofer lines distinctly. The light in question is therefore undoubtedly reflected sunlight, and not due to fluorescence. The similarity of the appearances observed to those shown by Tyndall's "blue cloud," led the author to very carefully compare the light in question with that undoubtedly reflected from solid matter in a very fine state of division. A suitable reflecting medium was prepared by diluting French polish with fifty times its bulk of methylated spirit, and then adding a few drops of this solution to a glass of water. The fine precipitate of shellac thus obtained remains in suspension for days. This medium showed very clearly the property, characteristic of solid matter in a very fine state of division, that all light reflected from it at right angles to the line of incidence is completely polarised. When similarly examined, the spot of light on the candle flame showed exactly the same appearances. If looked at through a Nicol placed in the plane at right angles to the mean path of the sun's rays, the spot was clearly visible when the crystal coincided with the line of incidence, and vanished when it crossed it at right angles. With the aid of the spectroscope, it was found that all parts of the spectrum were polarised alike. The above results were obtained when the sun's

image was focussed on the centre of the flame. The bottom of the flame reflected only the more refrangible rays as far as the middle of the green; towards the apex the red was also reflected: but in all cases the light was polarised.

When the spot and flame were examined in the spectroscope, and some soda-vapour allowed to pass into the flame, the bright D line was seen to cross the continuous spectrum of the candle, but to become reversed in the spectrum of the spot, all the Fraunhofer lines, including the D line, being perfectly black. If a spirit-lamp is substituted for the candle in this experiment, the flame seems to the eye to disappear in the glare, and nothing but the bright sodium band is visible in the spectroscope. The flame of a Bunsen behaved similarly to the spirit-lamp. When sunlight was made to pass through the flame of a candle, and then examined spectroscopically, a very definite general absorption took place, which was most noticeable about F and G, where the spectrum of the reflected sunlight was brightest, and where in candle-light the rays are deficient. The more refrangible rays are most absorbed, and the absorption becomes greater as the smoky part of the flame is approached.

It is not possible to obtain an image of one candle flame on another of a like character, but if the temperature of the recipient flame be lowered (for instance by holding an iron nail in it), the image of the other at once becomes visible, but is of a dirty yellow colour, instead of the bluish-white of that obtained with sunlight. The column of smoke obtained by lowering a tin plate, with a small hole in the centre, on to the flame of a candle, reflects and polarises either candle- or sun-light. An apparently similar column of smoke, produced by placing some paraffin on the hot plate, *did not polarise* the reflected light. The soot deposited on the under side of the tin plate polarised light reflected from it at right angles to the line of incidence.

By using a Bunsen burner with a rectilinear aperture, and allowing two sides of the flame to impinge on two glass plates, the author was enabled to examine the inner and outer flames separately. A mixture of copper sulphate and ammonium chloride burns in the inner flame, and reflects and polarises sunlight. Zinc when distilled in the inner flame does not reflect or polarise light, but as soon as the vapour reaches the outer flame and becomes oxidised to non-volatile zinc oxide, white light is produced which gives a continuous spectrum, and both reflects and polarises sunlight.

From these experiments, the author concludes that the luminosity of the ordinary flame is due to minute solid particles present therein. He suggests that the polarisation test is a good means of distinguishing between "vapour" however dense and true "smoke." He is still continuing these experiments. L. T. T.

**Indices of Refraction of Liquefied Gases.** By L. BLEEKRODE (*Proc. Roy. Soc.*, 37, 339—362).—In this paper, a description is given of the apparatus used for inclosing the liquefied gases between parallel glass plates, and of applying the microscopical method for the determination of their indices of refraction. With a high magnifying ocular power and a feeble objective lens, well defined images could be

focussed on microscopic test objects, such as the scales of wings of the Lepidoptera fixed on glass plates, homogeneous sodium light being used for the experiments. In the table the results are given of the refractive indices of substances, both in the gaseous and liquid conditions, and for the constants of Gladstone  $\left(\frac{n-1}{d}\right)$  and Lorenz  $\left(\frac{n^2-1}{(n^2+2)d}\right)$

Substance.	Index of refraction.		$\frac{n-1}{d}$		$\frac{n^2-1}{(n^2+2)d}$	
	Liquid.	Gas.	Liquid.	Gas.	Liquid.	Gas.
Sulphurous anhydride....	1·351	1·00069	0·252	0·236	0·153	0·157
Cyanogen .....	1·327	1·00082	0·378	0·35	0·234	0·233
Hydrocyanic acid.....	1·264	1·00045	0·379	0·368	0·238	0·246
Nitrous oxide.....	1·204	1·0005	0·235	0·255	0·15	0·17
Carbonic anhydride.....	1·196	1·00044	0·227	0·221	0·145	0·147
Hydrogen chloride .....	1·257	1·00045	0·300	0·277	0·19	0·185
Chlorine .....	1·367	1·00077	0·27	0·24	0·169	0·16
Ammonia .....	1·325	1·00037	0·528	0·49	0·327	0·327
Ethylene .....	1·180	1·00067	0·498	0·526	0·321	0·350
Hydrogen phosphide.....	1·323	1·00079	0·519	0·5	0·322	0·333
Hydrogen sulphide.....	1·39	1·00064	0·429	0·413	0·262	0·275
Methylamine .....	1·342	—	—	—	—	—
Dimethylamine .....	1·35	—	—	—	—	—
Trimethylamine.....	1·353	—	—	—	—	—
Zinc ethyl.....	1·485	—	—	—	—	—
Zinc methyl.....	1·474	—	—	—	—	—
Aluminium methyl.....	1·432	—	—	—	—	—
Aluminium ethyl.....	1·48	—	—	—	—	—

Comparing the experimental result for the molecular refraction with the value deduced from Landolt and Gladstone's data,  $\frac{Mn-1}{d} = 0·321 \times 28 = 8·99$ , and  $2A\frac{n-1}{d}(C) + 4A\frac{n-1}{d}(H) = 4·86 + 4·08 = 8·94$ , the values are found to be approximately identical. Similarly on comparing the values of the haloid acids with those of the corresponding halogens, the mean value of hydrogen is concordant with that deduced from other substances. As the indices of refraction of the zinc and aluminium organo-metallic compounds are less than that of stannic chloride ( $\mu_B = 1·5225$ ) it does not necessarily follow that all substances with high indices of refraction are very combustible, a generalisation which has frequently been advanced. V. H. V.

**Duration of Colour Impressions upon the Retina.** By E. L. NICHOLS (*Amer. J. Sci.* [3], 28, 243—252.)

**New Form of Voltaic Battery.** By P. JABLOCHKOFF (*Proc. Roy. Soc.*, 36, 141—142).—In this paper, a battery is described in which the electropositive element is sodium, the electronegative element carbon,

spongy platinum, or copper; the action of the aqueous vapour of the atmosphere on the sodium producing a solution of soda, which is thus interposed between the sodium and the electronegative element. The E.M.F. of the cell is about 2.75 volts; a battery composed of plates  $10 \times \frac{1}{2}$  inch gave a current of 9.122 ampères at first, which after five minutes is reduced by polarisation to 0.079 ampère. V. H. V.

**Daniell's Cell of Small Internal Resistance.** By J. T. BOTTOMLEY (*Proc. Roy. Soc.*, **37**, 173—177).—In this paper a form of Daniell's cell is described, set up in such a manner that the copper and zinc sulphate solutions are supplied of constant strength by a number of syphon arrangements. When the battery is not in use the position of the syphon is reversed, and the solutions drained off. From this cell there was obtained, as indicated by a current galvanometer of 0.002 ohm resistance, a current of 63 ampères, which remained steady for a long interval of time. V. H. V.

**Electrochemical Equivalent of Silver.** By LORD RAYLEIGH and MRS. SIDGWICK (*Proc. Roy. Soc.*, **36**, 448—450, and **37**, 142—146).—In these papers, an account is given of experiments made with a view of determining the electrochemical equivalent of silver in terms of practical units. The final number expressed in C.G.S. units is  $1.118 \times 10^{-2}$ , a value in accordance with that determined by Kohlrausch; thus in practical units the quantity of silver deposited per ampère per hour is 4.0246 grams. With a view of obtaining a convenient standard of E.M.F., the authors have made a detailed examination of Clark's cells, which possess the advantage of standing ready for use, and not polarising greatly on the passage of small currents. The value for the E.M.F., that of the B.A. unit being 0.9867 ohm, is equal to 1.435 volt, with an extreme range of  $\frac{1}{1000}$  during six months, although about ten days are required before the cell reaches its permanent condition. V. H. V.

**Influence of Light on the Electrical Resistances of Metals.** By A. E. BOSTWICK (*Amer. J. Sci.* [3], **28**, 133—145).—From a series of elaborate experiments made in the Yale College Laboratory on plates of platinum, gold, and silver, the author concludes that if light causes any diminution in the electrical resistance of metals, it probably does not exceed a few thousandths of 1 per cent. B. H. B.

**Variation in the Electrical Resistance of Bismuth when placed in a Magnetic Field.** By HURION (*Compt. rend.*, **100**, 348).—When a plate of bismuth is placed in a magnetic field in a direction normal to the lines of magnetic force, the resistance of the bismuth increases more rapidly than the intensity of the magnetic field, as Righi has previously observed, and the increase is proportional to the mechanical effect exerted on the bismuth by the electromagnet. C. H. B.

**Pyroelectricity of the Topaz.** By C. FRIEDEL and J. CURIE (*Compt. rend.*, **100**, 213—219).—The authors experimentally cleaved fragments of yellow Brazilian topaz, and confirm Friedel's earlier observation

that in topaz the principal axis of pyroelectricity is parallel with the edges of the prism. Many fragments show poles of the same sign at both ends, but in such cases the fragment can be cleaved into two parts, the bases of which will have opposite polarity. In one instance, one extremity of the fragment was bounded by the natural summit of the crystal and the other extremity by a cleavage plane, and both ends showed negative electricity when cooled. When this fragment was cleaved at the middle, one half showed regular polarity, whilst the other half was still negative at both ends but with different intensities. These results are explained by the existence of twinning parallel with the base of the prism.

With colourless rounded Brazilian topaz, the pyroelectricity was much less marked, and with certain sections was almost imperceptible. Frequently both terminations have the same sign, but in many cases the removal of a very thin layer changes the sign of one termination and produces fragments with regular polarity.

Optical examination shows that the topaz crystals are not homogeneous, but in many cases can be separated into four distinct portions along the diagonals of the rhombic base. Generally, however, these four parts enclose an inner rhombic prism with regular extinction, and the crystal can consequently be split up into five distinct portions which, however, are still not homogeneous. From some larger crystals in which the planes of twinning were very distinct, the authors were able to obtain homogeneous fragments and to establish the existence of a horizontal axis of electricity, but the specimens were not sufficiently large to enable them to determine the exact direction of this axis. The existence of the horizontal axis was confirmed by the development of electricity under pressure (Abstr., 1881, 338—339).  
C. H. B.

**Electric Qualities of Glass.** By T. GRAY, A. GRAY, and J. J. DOBBIE (*Proc. Roy. Soc.*, **36**, 488—498).—Although the correlation between the composition of glass and its conductivity has not been much studied, yet previous observations seem to show that a greater proportion of alkali decreases, while that of lead oxide increases the resistance. The lead or flint glasses, are herein more completely examined. The method of experiment, in outline, consisted in immersing a small flask of the glass to be examined, and filled with mercury, into a larger vessel also containing mercury. The mercury within and without the experimental flask is connected through a sensitive galvanometer with a battery of Daniell's cells. The following table contains the results obtained for the density, specific resistance in ohms, percentage proportion of lead oxide, and the formula expressing approximately the chemical composition:—

	Sp. gr.	Sp. resistance.	P.c. lead oxide.	Formula.
1.	3.145	$4700 \times 10^{10}$	37.098	$80\text{SiO}_2, 15\text{PbO}, 3\text{K}_2\text{O}, 2\text{Na}_2\text{O}.$
2.	3.141	$8400 \times 10^{10}$	40.55	$22\text{SiO}_2, 5\text{PbO}, 2\text{K}_2\text{O}, \text{Na}_2\text{O}.$
3.	3.141	$3868 \times 10^{10}$	36.98	$61\text{SiO}_2, 12\text{PbO}, 7\text{K}_2\text{O}, 2\text{Na}_2\text{O}.$
4.	2.811	$453 \times 10^{10}$	19.87	$24\text{SiO}_2, 2\text{PbO}, 3\text{K}_2\text{O}, \text{Na}_2\text{O}.$
5.	3.018	$545 \times 10^{10}$	17.89	$48\text{SiO}_2, 4\text{PbO}, 5\text{K}_2\text{O}, 5\text{Na}_2\text{O}.$
6.	2.829	$85 \times 10^{10}$	21.42	$10\text{SiO}_2, \text{PbO}, \text{K}_2\text{O}, \text{Na}_2\text{O}.$

The general result to be drawn from a comparison of these data is, that the specific resistance of the glasses increases alike with the percentage of the lead oxide and also with the density; and further, *cæteris paribus*, an increase of proportion of alkali diminishes the resistance, although its effect is not so marked as the opposite effect of lead oxide.

It is further suggested as possible that, in the case of those glasses which have approximately the same composition, but differ in density, those with higher density approach more nearly to a definite composition. It is proposed to extend these experiments to crystalline minerals, and to trace out relations between their electrical quality and their crystallographic axes.

V. H. V.

**Measurement of Rapidly Alternating Electric Currents with the Galvanometer.** By L. M. CHEESMAN (*Amer. J. Sci.* [3], 28, 117—121).

**Simple Form of Thermo-regulator and Registering Thermo-meter combined.** By E. H. v. BAUMHAUER (*Zeits. Anal. Chem.*, 25, 42—46).

**Heat of Formation of Ammonium Sulphite and Bisulphite.** By FORCRAND (*Compt. rend.*, 100, 244—247).—The neutralisation of sulphurous anhydride ( $\text{SO}_2 = 64$  grams) by one equivalent of ammonia ( $\text{NH}_3 \cdot \frac{1}{2} \text{H}_2\text{O} = 26$  grams) develops + 14.78 cal.; by two equivalents ( $\text{NH}_4\text{O} = 52$  grams) + 25.4 cal. The presence of excess of ammonia causes very little further development of heat.

*Normal ammonium sulphite*,  $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ , is obtained in bulky colourless crystals by neutralising concentrated aqueous ammonia with sulphurous acid and allowing the liquid to cool. Heat of solution of the hydrated salt (liquid) = - 2.68 cal. at  $-8^\circ$ ; of the anhydrous salt - 0.77 cal. at  $8^\circ$ , hence  $(\text{NH}_4)_2\text{SO}_3$  solid +  $\text{H}_2\text{O}$  liquid =  $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$  solid, develops + 3.82 cal.; +  $\text{H}_2\text{O}$  solid, develops + 2.38 cal., from which it follows that—

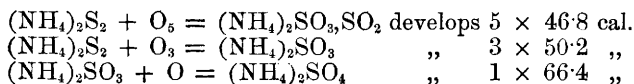
S solid + $\text{O}_3$ gas + $\text{H}_8$ gas + $\text{N}_2$ gas =	
$(\text{NH}_4)_2\text{SO}_3$ solid .....	develops + 215.44 cal.
S gas + $\text{O}_3$ gas + $\text{H}_8$ gas + $\text{N}_2$ gas =	
$(\text{NH}_4)_2\text{SO}_3$ solid .....	„ + 218.00 „
$\text{SO}_2$ gas + $2\text{NH}_3$ gas + $\text{H}_2\text{O}$ gas =	
$(\text{NH}_4)_2\text{SO}_3$ solid .....	„ + 64.8 „

*Ammonium bisulphite (metasulphite)*,  $(\text{NH}_4)_2\text{SO}_3 \cdot \text{SO}_2$ , is obtained in large crystals by saturating concentrated aqueous ammonia with sulphurous anhydride. Heat of solution (liquid) = - 3.19 cal. at  $8^\circ$ , hence—

$\text{S}_2$ solid + $\text{O}_5$ gas + $\text{H}_8$ gas + $\text{N}_2$ gas =	
$(\text{NH}_4)_2\text{SO}_3 \cdot \text{SO}_2$ solid .....	develops + 300.0 cal.
$\text{S}_2$ gas + $\text{O}_5$ gas + $\text{H}_8$ gas + $\text{H}_2\text{O}$ gas =	
$(\text{NH}_4)_2\text{SO}_3 \cdot \text{SO}_2$ solid .....	„ + 305.2 „
$2\text{SO}_2$ gas + $2\text{NH}_3$ gas + $\text{H}_2\text{O}$ gas =	
$(\text{NH}_4)_2\text{SO}_3 \cdot \text{SO}_2$ solid .....	„ + 80.0 „

The action of 2 mols. ammonia on 1 mol. metaspulphite develops + 20.74 cal.

From these values and the values given by Sabatier for the heats of formation of the sulphides, the following results can be deduced :—



The corresponding numbers in the case of potassium are—

$$5 \times 52.6 \qquad 3 \times 56.8 \qquad 1 \times 69.6 \text{ cal.}$$

and of sodium—

$$5 \times 51.4 \qquad 3 \times 57.6 \qquad 1 \times 65.4 \text{ ,,}$$

C. H. B.

**Thermic Data for the Compounds of Aluminium Bromide with Hydrocarbons.** By G. GUSTAVSON (*J. Russ. Chem. Soc.*, 1885, 57).—The heat of dissolution of a molecule of  $\text{Al}_2\text{Cl}_6$  was found to be 153,739 cal. (Thomsen 153,690, Berthelot 152,600); the number for  $\text{Al}_2\text{Br}_6$ , the average for six determinations, is 180,237 (Berthelot, 170,600). The compound of aluminium bromide with toluene, if dissolved in water, develops heat equivalent to somewhat more than 168,000 cal. (average of five experiments); the formation of this compound is consequently accompanied by development of heat. With the compounds of aluminium bromide and fatty radicles the difference appears to be even greater, the heat of dissolution of the compound,  $\text{AlBr}_3, \text{C}_7\text{H}_8$ , being 145,000—150,000 cal.; but these experiments are not considered conclusive by the author. A. T.

**Calorific Power of Coal-gas in Various States of Dilution.** By A. WITZ (*Compt. rend.*, 100, 440—441).—The heat of combustion of 1 cubic metre of well-purified coal-gas, saturated with aqueous vapour and mixed with six times its volume of air, is about 5200 cal. Before passing through the scrubber and purifier the same gas gave 5600 cal.

If the amount of heat developed by a mixture of 1 vol. of coal-gas with 6 vols. of air is taken as the unit, the heat developed is increased 5 per cent. when the coal-gas is mixed with 2.25 vol. of oxygen, but diminished 4.6 per cent. when it is mixed with 11 vols. of oxygen. It follows, therefore, that the calorific power of coal-gas is diminished by dilution with oxygen.

If 1 vol. of gas is mixed with 10 vols. of air, the heat developed is increased by 2.5 per cent., and hence it would seem that 6 vols. of air are not sufficient for the complete combustion of 1 vol. of coal-gas.

C. H. B.

**Chemical Neutrality of Salts, and the Use of Different Indicators in Acidimetry.** By BERTHELOT (*Compt. rend.*, 100, 207—213).—The author shows that the recent observations of Joly and others on the behaviour of different indicators towards acids and salts is in agreement with known thermochemical data relating to the

action of acids on the salts in question, and the dissociation of salts in solution.

The difference between the colour of normal potassium chromate and the dichromate is so well marked that the latter may be employed as an indicator. It behaves similarly to helianthine A.

C. H. B.

**Laws of Dissolution.** By H. LE CHATELIER (*Compt. rend.*, **100**, 441—444.)—The author has previously shown (*Compt. rend.*, **100**, 50) that the relation between the coefficient of solubility of salts, their heat of dissolution at saturation, and the temperature, may be approximately expressed by the equation—

$$\frac{dx}{x} = \frac{k}{\delta} Q \frac{dt}{T^2},$$

from which it follows that  $\frac{dx}{dt}$ , the variation of the coefficient of solubility, is of the same sign as  $Q$ , the quantity of heat gained by the dissolution; or, in other words, if the dissolution of a substance is accompanied by absorption of heat, the solubility of that substance will increase with the temperature and *vice versa*, whilst if the dissolution of a substance neither develops nor absorbs heat its solubility will be independent of the temperature.

Cases of substances which dissolve with absorption of heat, and become more soluble as the temperature rises are very numerous; but solids which dissolve with development of heat and become less soluble with increase of temperature are much rarer, the only substances which exhibit these phenomena being calcium hydroxide, cerium sulphate, and anhydrous sodium sulphate. There is no well established instance of a solid which dissolves without thermal disturbance, although Berthelot has found that this is the case with calcium sulphate in supersaturated solution at 23.7°, and Marignac has shown that the maximum solubility of this salt is at 35°.

Amongst liquids examples of dissolution with development of heat, and decrease of solubility with an increase in temperature, are furnished by bromine and water, ether and water, and carbon bisulphide and water, and it is well known that gases dissolve with development of heat, and that their solubility decreases as the temperature rises.

The dissolution of liquids constitutes a special case, since either of the substances may be regarded as the solvent, according to the conditions.

If A and B are the two liquids,  $\frac{b}{a}$  the coefficient of solubility of B

in A, and  $\frac{a'}{b'}$  the coefficient of solubility of A in B, then if A and B

are mixed in a proportion lower than  $\frac{b}{a}$  or higher than  $\frac{a'}{b'}$ , solution

will be complete with formation of a homogeneous non-saturated liquid, but with any intermediate proportions two saturated solutions will be formed, separated by reason of their difference of density. If the temperature varies, the two coefficients of solubility will vary (in



the case of ether and water, which dissolve with development of heat, the coefficients will diminish with a rise of temperature), and consequently the difference between the composition of the two saturated solutions will continually diminish until one coefficient is the inverse of the other, and at this temperature, and at all lower or higher temperatures, as the case may be, the two liquids will be perfectly miscible, and it will be impossible to obtain distinct saturated solutions. Nicotine and water are miscible in all proportions at the ordinary temperature, but at about 100° the liquid separates into two layers. This phenomenon points to a diminution of solubility, hence to development of heat on dissolution, and the author finds that the dissolution of nicotine in water is accompanied by a rise of temperature. There is no essential difference between liquids which are miscible and those which are not; it is merely a question of the coefficient of solubility and the temperature. Pictet has found that liquid carbonic anhydride and liquid sulphurous anhydride are miscible in all proportions at the ordinary temperature, but the mixture separates into two layers at a lower temperature. The homogeneous mixture has a lower vapour-tension than the two liquids superposed, and Pictet concludes that since the mixture of these two substances requires a lower pressure to liquefy it, the use of such a mixture will increase the efficiency of freezing machines. From the above considerations, however, it follows that the separation of the liquid into two layers indicates a decrease in solubility with a decrease in the temperature, and points to absorption of heat during dissolution. Consequently, during the evaporation of the mixed liquids less heat will be absorbed than by the two liquids separately, and this diminution in the amount of heat absorbed will compensate for the lower pressure required to produce liquefaction.

C. H. B.

**Boiling of Liquids in a Vessel Contained in a Water-bath.** By C. TOMLINSON (*Proc. Roy. Soc.*, **37**, 113—114).—Writers of the last century have remarked upon the apparently paradoxical phenomenon that water immersed in a vessel containing boiling water cannot be made to boil, the temperature being always some few degrees below that of the latter. This result the author shows to be evidently due to evaporation, for on covering the water in the inner vessel with oil the temperature rises to the boiling point, and bubbles of steam escape from the surface of the water through the oil.

V. H. V.

**Dissociation of Chlorine Hydrate.** By H. LE CHATELIER (*Compt. rend.*, **99**, 1074—1077).—The well-known equation representing the relation between the temperature and the tensions of evaporation and dissociation—

$$\frac{E}{T} \frac{Q}{s - \sigma} = \frac{dp}{dt},$$

where  $Q$  and  $S - \sigma$  represent respectively the heat developed and the change of volume produced by the transformation of the same quantity of matter, indicates that when the value of  $Q$  changes

suddenly by reason of a progressive rise of temperature, as when one of the bodies passes its melting point,  $\frac{dp}{dt}$ , that is, the angular coefficient of the tangent to the curve of pressures, changes equally suddenly. This phenomenon has not hitherto been actually observed, because the vapour-tension and heat of fusion of solids is usually too small. The phenomenon is, however, clearly shown by chlorine hydrate,  $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ , which has a considerable tension of dissociation even at  $0^\circ$ , and the heat of formation of which varies by 7.15 cal., according as it is formed from liquid or solid water.

When chlorine hydrate is gradually cooled in an atmosphere of chlorine, the tension diminishes regularly down to a temperature which varies in different experiments, but generally lies between  $-4^\circ$  and  $-7^\circ$ . At this point, the tension suddenly increases to about 0.2 m., then rapidly diminishes and becomes stationary at a point somewhat higher than its value before the disturbance. On further cooling, the pressure diminishes regularly. The observed phenomenon is due to the sudden solidification of the water, which was in superfusion. The change of state causes a rise of temperature which produces a corresponding increase of pressure. Equilibrium of temperature being established, the tension of the chlorine acquires the normal value corresponding with the dissociation of the chlorine hydrate with liberation of solid water, this value being higher than when the hydrate dissociates into chlorine and liquid water.

If the chlorine hydrate is heated, the tension increases regularly up to about  $-1^\circ$ , at which point the temperature remains stationary during the melting of the ice. No sudden alteration of pressure is observed, and this indicates that the passage from the solid to the liquid state at the *temperature of equilibrium* produces no appreciable change in the tensions of dissociation, any more than in vapour-tensions.

The curves corresponding respectively with dissociation into chlorine and solid water, and into chlorine and liquid water, differ from one another by a considerable angle. The difference between the heats of formation of the chlorine hydrate from solid and liquid water respectively, as calculated from the equation and these curves, is 8.3 cal., a number which approaches closely to the actual difference, 7.15 cal.

C. H. B.

**Solidification of Nitrogen and Carbonic Oxide: Relation between the Temperature and Pressure of Liquid Oxygen.** By K. OLSZEWSKI (*Compt. rend.*, 100, 350—352).—Alterations in the arrangement of the manometers enable the author to measure accurately pressures as low as 4 mm. Temperatures are measured with a hydrogen thermometer.

*Nitrogen.*—Under a pressure of 60 mm., liquid nitrogen solidifies, the temperature during solidification being  $-214^\circ$ , and by further reduction of the pressure the whole of the nitrogen can be solidified to a snow-like mass. Under a pressure of 4 mm. the solid nitrogen has a temperature of  $-225^\circ$ , the lowest temperature that has yet been measured. It is probable that the actual temperature is even

lower than this, since the bulb was not completely surrounded by the solid nitrogen.

*Carbonic Oxide.*—The gas used was prepared by the action of sulphuric acid on formic acid. Under a pressure of 100 mm. liquid carbonic oxide begins to solidify, its temperature being  $-207^{\circ}$ . Under still lower pressure, with a temperature of  $-211^{\circ}$ , the whole of the carbonic oxide solidifies to a snow-like mass. Under a pressure of 4 mm., the temperature of the carbonic oxide is  $-220.5^{\circ}$ .

*Oxygen.*—The following results were obtained :—

Pressure. atmos.	Temperature.	Pressure. atmos.	Temperature.
50.8 (crit. pres.)	$-118.8^{\circ}$ (crit. temp.)	13.7	$-146.8^{\circ}$
49.7	$-119.5$	12.3	$-148.6$
47.6	$-120.7$	10.24	$-151.6$
46.7	$-121.6$	8.23	$-155.6$
45.5	$-122.6$	6.23	$-159.9$
43.0	$-124.0$	4.25	$-166.1$
40.4	$-125.6$	2.16	$-175.4$
38.1	$-126.8$	1.0	$-181.4$
36.3	$-128.0$	9 mm.	$-211.5$
34.4	$-129.0$	4 mm.	still liquid.
32.6	$-130.3$		

The author was unable to measure the temperature under a pressure of 4 mm., because the quantity of oxygen was not sufficient to cover the bulb of the thermometer. Although the oxygen was still liquid the temperature must have been much below  $-211.5^{\circ}$ .

C. H. B.

**Attraction between a Dissolved Solid and a Substance Immersed in the Solution.** By J. THOULET (*Compt. rend.*, 99, 1072—1074).—When marble, kaolin, quartz, or other inert substance is immersed in a solution of sodium or barium chloride, the amount of salt in solution decreases, owing to the deposition of a portion of the dissolved salt on the surface of the immersed solid. If a piece of dry white marble is weighed first in alcohol of known sp. gr., and then in a concentrated solution of potassium carbonate of known sp. gr., the weight in the latter is always greater than that calculated from the ratio of the two specific gravities, because some of the potassium carbonate is deposited on the surface of the marble. Further, if grains of quartz or glass, varying in diameter from 0.15 mm. to 0.9 mm., are placed in solutions of iodides, the sp. gr. of the latter can be adjusted so that the smaller particles will sink whilst the larger will swim. This result is due to the fact that the surface is greater in proportion to the total volume in the case of small particles than in the case of the larger ones, and hence a greater proportion of the dissolved salt is deposited in the first case than in the second. Marble is so porous that its surface is almost proportional to its volume, and consequently grains of marble do not show this phenomenon.

As the result of these and similar experiments, the author concludes that there is attraction between a dissolved salt and a solid immersed

in the solution, and that the amount of attraction is proportional to the surface of the immersed solid. These results explain the impurity of precipitates, the clarification of liquids by colloids, the purification of water by natural filtration, &c.

C. H. B.

**Condensation of Gases on the Surface of Glass.** By J. T. BOTTOMLEY (*Chem. News*, 51, 85).—The following experiment was conducted in order to determine the quantity of gas condensed on a given surface of glass. A quantity of glass fibre (drawn from flint-glass rod) exposing a surface of 1448 sq. c.m., was put into a glass tube attached to a Sprengel pump, this was worked until the pressure gauge was constant at 0.3 M; heat was now applied to the tube containing the fibres; the pressure rose immediately, and the gas given off was collected. The heating and pumping were continued for more than an hour, when the pressure registered was 1.2 M. The quantity of gas collected in this manner was 0.45 c.c. at 15° and 760 mm., and when analysed in the usual manner gave: 8.24 per cent. CO<sub>2</sub>; 24.80 O; 75.2 N.

D. A. L.

**Separation by Capillary Attraction.** By J. U. LLOYD (*Chem. News*, 51, 51—54).—It has been shown that substances can be separated from their solutions by capillary attraction. Bayley (*Trans.*, 1878, 304—306) let drops of certain solutions fall on filter-paper, and observed that sometimes the salt remained in the centre, whilst a water-ring extended round it; and by means of hydrogen sulphide he traced the extent of the diffusion of metallic salts, whilst alkaline solutions were tested on turmeric paper. He showed that the greater the dilution the broader is the water-ring; whilst concentration, heat, and looseness of the texture of the paper are favourable to the mobility of the substance in solution. Also that the metals differed in their degrees of mobility, and in mixed solutions acted independently of one another; also that acidity increased the mobility of copper. The author allows strips of blotting-paper to dip into various solutions, and observes the distance the substances in solution extend on the paper before they are left behind by the water, and his observations confirm Bayley's results. For example, syrupy solutions of ferric sulphate travel with the water some distance on the paper, and no separation takes place, then a series of experiments show the decreasing mobility of the metallic salt as the solutions are less concentrated, whilst the water separates more and more; ultimately with very dilute solutions the metallic salt creeps just above the surface of the solution, whilst the pure water continues its course to the end of the paper (5 inches). Similar experiments were made with other salts, proving the great difference in the mobility of different metals, for example, sodium chloride was carried six feet without showing signs of separation. The independent activity of metallic salts in solutions containing mixtures of them is also confirmed by the present experiments; they even behave quite regularly in dilution experiments, and always show a clear and sharp boundary line between each salt and between the most mobile salt and the pure water; for example, solutions of equal strength, of ferrous sulphate, copper

sulphate, and ferric sulphate, were experimented on separately, and mixed together, and in solutions of different but always proportional strengths, in all cases the ferrous sulphate showed the same line of demarcation for a certain strength, being more mobile than the copper sulphate, which was also constant in a similar manner, and more mobile than the ferric salt. Bayley remarks (*loc. cit.*) that silver, lead, and mercuric salts, when moderately concentrated, give a wide water-ring, whilst copper, nickel, and cobalt salts need greater dilution to produce the same appearance; cadmium seems especially mobile. In solutions containing sulphate of quinine and sulphate of berberine, the former salt passes onwards, leaving the latter behind. Dilute sulphuric acid behaves in a similar manner, perfectly non-acid water passing onwards. By allowing a strip of blotting-paper to dip into a solution of ferric sulphate, then curving it over a sufficient height, and letting the other end hang below the level of the solution, after some time water absolutely free from iron drops from the further end of the paper. Some quantitative experiments have also been made. In a solution containing 1 part of ferric sulphate in 32 parts of water, the water extended 5 inches on the paper, the iron solution 2 inches, the paper was divided on the point of separation, and at the surface of the liquid. Both pieces of wet paper were weighed, then dried, and again weighed. The piece of paper containing the iron contained 7 parts of water, the other piece  $7\frac{1}{2}$  parts. In a solution of half this strength tested in a similar manner the piece of paper containing iron gave up 4 parts, the other piece  $9\frac{1}{2}$  parts of water. Similar experiments with lead acetate confirm this result, thus giving quantitative evidence showing that the more dilute the solution the quicker the separation and the greater the mobility of the water, and *vice versa*. D. A. L.

**Rate of Propagation of Detonation in Solid and Liquid Explosives.** By BERTHELOT (*Compt. rend.*, 100, 314—320).—In order to determine the rate of transmission of the explosive wave in solid and liquid explosives, the latter were detonated in tubes of lead, tin, or Britannia metal, 1—2 mm. in internal diameter, and 100 to 200 metres long. The explosives employed were pulverulent or granulated gun-cotton, xyloidin, nitromannitol, nitroglycerol, dynamite, and pancastite. The results show that as a rule the rate of propagation of the explosive wave increases with the density of the charge, and also, for tubes of the diameters employed, with the diameter of the tube. It also seems to increase with the resistance of the material of which the tube is composed. The detonation shatters the tube in which the explosive is contained, and in this respect the experiments differ from those in which the explosives are gaseous. The results were sensibly the same whether the tubes were bent or straight.

With compressed pulverulent gun-cotton, the mean velocity of the explosive wave is about 5200 m. per second in lead tubes, and about 6000 m. per second in tin tubes. Granulated gun-cotton with a density of 1.1—1.3 gave a velocity of about 5000 m. Xyloidin gave similar results. Nitromannitol gives a still higher velocity, granulated nitromannitol of density 1.9, giving the highest observed

velocity, 7686 m. per second. With nitroglycerol in tubes 3 mm. diameter the rate of transmission is much lower, and varies between 1078 and 1386 m. according to the conditions. Dynamite in tubes 3 mm. in internal diameter gave a velocity of 2333—2753 m., and in tubes 6 mm. diameter an average of 2668 m. Panclastite gave results similar to those obtained with gun-cotton. C. H. B.

**Conditions of Chemical Change in Gases.** By H. B. DIXON (*Proc. Roy. Soc.*, 37, 56—61).—Bunsen concluded from his experiments on mixtures of carbonic oxide and electrolytic gas in various proportions, that the general law of mass was in this particular instance modified by the tendency to formation of simple hydrates of carbonic anhydride. Thus the ratio of carbonic oxide to hydrogen could be varied within certain limits without altering the proportion in which the oxygen divides itself between these gases, but a still greater change of the relative proportions induces a change *per saltum* of the division of oxygen. In the year 1876, Horstmann and the author independently came to the conclusion that Bunsen's results were vitiated by the presence of aqueous vapour. In connection with these experiments, it was shown that a dry mixture of carbonic oxide and oxygen is not ignited by an electric spark (comp. Abstr., 1883, 12), and that an imperfectly dry mixture is unaffected at pressures below 510 mm., and when under higher pressures burns slowly. The part played by steam in inducing the combination of carbonic oxide with oxygen is thus analogous to that of the nitric oxide in the sulphuric acid chamber, in that it undergoes a succession of alternate reductions and oxidations. Experiments are also described on the mean rate of explosion of carbonic oxide and oxygen with different quantities of aqueous vapour under atmospheric pressure, the explosion-tube being 1 metre in length. As a general result it may be stated that the velocity of explosion increases with the proportion of aqueous vapour. A comparison of the experiments on the explosion of dry carbonic oxide and electrolytic gas shows that the division of oxygen was affected not only by changes in the initial pressures of the gases, but also by the temperature and shape of the containing eudiometer. With increasing pressure, more steam and less carbonic anhydride are formed in the explosion. When the pressure is increased to a certain amount, which varies with different mixtures, no further increase of pressure alters the ratio of the products formed. With pressures above the "critical pressure," changes in the shape of the vessel also cease to affect the ratio of the products. As at ordinary temperatures condensation of steam occurs during the reaction, the temperature at which the experiments were performed was sufficiently high to prevent this condensation. When dry mixtures of carbonic oxide and hydrogen in various proportions are exploded above the critical pressures with a quantity of oxygen insufficient for their complete combustion, an equilibrium is established between two opposite chemical changes, expressible by the equations (1)  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$  and (2)  $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$ , so that at the end of the reaction the product of the carbonic oxide and steam molecules is equal to the product of the carbonic anhydride and hydrogen mole-

cules multiplied by a coefficient of affinity. The presence of an inert gas, such as nitrogen, by diminishing the intensity of the reaction, favours the formation of carbonic anhydride in preference to steam. When the hydrogen is less than double the oxygen, the excess of oxygen cannot react with any of the three other gases present—carbonic oxide and anhydride and steam—and herein, as inert, would have the same effect as the nitrogen in favouring the formation of carbonic anhydride. Within the limits detailed above, the law of mass is verified for the gaseous system composed of carbonic oxide and anhydride, hydrogen, and steam, at a high temperature.

V. H. V.

**The Influence of the Diluent, and the Action of Excess of the Ingredients, on the Rate of Chemical Action.** By F. URECH (*Ber.*, 18, 94—102).—In this communication, the author carefully discusses the facts at present known as to the influence of dilution and of excess of one or other ingredient on the rate of chemical action. He comes to the conclusion that when the diluent acts purely as such, it does not influence the rate of reaction. Excess of one ingredient, however, has a decided influence, and this influence is different according to which ingredient is in excess. In the case of the reduction of Fehling's solution with dextrose, for instance, increasing the equivalent proportion of dextrose from 1 to 3 causes an increase in the rate of reduction of more than threefold, whereas a similar increase of Fehling's solution from 1 to 3 equivalents only increases the rate of reaction by a little more than a half. The author therefore comes to the conclusion that the reaction-equations proposed by Guldberg and Waage are incorrect, and that the causes of variation in rate of reaction are exceedingly complicated, and are probably much influenced by molecular friction, the velocity and length of path of the molecules, the caloric and electric conductivity, &c., and even by the shape and character of the containing vessel.

L. T. T.

**Action of Mass.** By W. SPRING (*Ber.*, 18, 344—346).—The author brings forward a number of experiments showing the influence of mass on chemical reactions, which, although incomplete (the researches having had to be abandoned) are yet of value as confirming the conclusions deduced by Potilitzin from his experiments on the displacement of chlorine by bromine (*Abstr.*, 1884, 955).

A. J. G.

**Rate of Formation of the Carbonates of the Alkaline Earths in relation to Time, Mass, and Nature of the Bodies used for Precipitation.** By J. BEVAD (*J. Russ. Chem. Soc.*, 1885, 89).—The experiments were conducted as follows:—Solutions of the chlorides of calcium, strontium, or barium were poured into solutions of the alkaline carbonates (Li, K, Na) in such a manner that in using 40 c.c. of the chlorides the whole of the liquid was in each instance 78·5 c.c.; the liquid was then filtered either at once (the reaction lasting about five minutes), or after 30—60 minutes, or after 24 hours. The carbonates and the chlorides were taken in equivalent quantities, the relation being 1 : 1, 2 : 1, 3 : 1, or 4 : 1. The re-

sults are summed up in a table. In the first period (five minutes) the speed of formation of the carbonates is the greatest; it increases at the same rate as the quantity of the insoluble salt formed—(1) as the concentration of the salt used for precipitation increases; (2) in the direction from Li to K; (3) from Ca to Ba. The average speeds for the consecutive periods exhibit an inverse relation: they decrease rapidly—(1) with the increase of the concentration of the alkaline carbonates; (2) in the direction from Li to K; and (3) from Ca to Ba.

A. T.

**A Particular Case of Catalytic Action.** By LORIN (*Compt. rend.*, 100, 282—284). A controversial paper containing no new facts.

C. H. B.

**Apparatus to Determine the Equivalents of Certain Elements.** By H. N. MORSE and E. H. KEISER (*Amer. Chem. J.*, 6, 347—351).—This is an apparatus to enable a student to determine with sufficient accuracy the equivalent of certain metals in terms of hydrogen, by measuring the amount of hydrogen evolved on treating a weighed quantity of zinc or aluminium with dilute sulphuric acid. This apparatus has furnished very satisfactory results in the hands of students.

J. K. C.

**Laboratory Apparatus.** By H. LANDOLT (*Ber.*, 18, 56—57).—1. A combination of a water-bath with a hot-water funnel. 2. An apparatus for concentrating dilute solutions; it consists of a long flat rectangular metallic case, the upper surface of which has a rim round it, is corrugated, and either silvered or covered with thin platinum foil. The case stands on three legs, one of which has an adjustable screw, so that one end of the case may be raised higher than the other. It is partly filled with water, which is heated by a lamp placed at the lower end: the steam escapes by an opening in the side near the upper end. The liquid to be concentrated is allowed to drop on to the upper end of the corrugated surface, and in flowing down is compelled to pass over a very large heated surface. 3. An apparatus for sublimations, which consists in a platinum tube 150 mm. long and 18 mm. wide, closed at one end, and filled with water. The other end is fitted with a double-bored india-rubber stopper, through which glass tubes pass, enabling a constant current of cold water to be maintained. This apparatus is introduced into the neck of the vessel in which the substance is being heated, and forms a cold surface on which the vapour of the substance condenses.

L. T. T.

**New Forms of Laboratory Apparatus.** By E. HART (*Amer. Chem. J.*, 6, 178—180).—I. *Apparatus for Fractional Distillation.*—Instead of the ordinary three-way tube for connecting the flask with the condenser, a tube is used to which is adapted a side tube some 2 feet in length and bent several times in a zig-zag form, its action being similar to that of the bulbs in a Le Bel-Henninger tube.

II. *A Valve for Use in Standardising Permanganate.*—This consists of a tube sealed at one end with a small hole in the side; the tube passes through a hole in the cork, and during the evolution of the gases produced in dissolving the iron in sulphuric acid, the hole stands above the cork. When the solution is complete, the tube is pressed



down so that the side opening comes below the cork, and thus the entrance of air is prevented.

III. *A Retort and Receiver for Small Distillations*.—The retort is constructed out of a test-tube bent at right angles; the receiver, another test-tube, into which the mouth of the first fits.

P. P. B.

**Use of Steam in Chemical Laboratories.** By J. WALTER (*J. pr. Chem.* [2], 30, 410—416).

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## Inorganic Chemistry.

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**Estimation of Carbon in Ordinary Phosphorus.** By I. REMSEN and E. H. KEISER (*Amer. Chem. J.*, **6**, 153—155).—The authors have already drawn attention to the presence of carbon in phosphorus (Abstr., 1884, 771), and in this communication describe the method of estimating the amount of this substance. For this purpose, the phosphorus is oxidised by nitric acid (sp. gr. 1.2) in a retort, the gaseous products, after passing through a wash-bottle containing water, are led through a combustion-tube containing copper and copper oxide, and finally into wash-bottles containing baryta-water. The amount of carbonic anhydride formed is determined by collecting the barium carbonate and converting it into sulphate. In the construction of the apparatus the use of organic materials was carefully avoided, the different parts being connected by glass tubing and gypsum joints. Out of six determinations of carbon in phosphorus, the extremes were 0.026 per cent. and 0.111 per cent. P. P. B.

**Preparation of Phosphorus Trifluoride.** By H. MOISSAN (*Compt. rend.*, **100**, 272—275).—Phosphorus trifluoride can be obtained by allowing arsenic trifluoride to drop into perfectly dry phosphorus trichloride. The product contains small quantities of arsenic fluoride and phosphorus trichloride, and attacks mercury. It is purified by shaking with a small quantity of water and drying over sulphuric acid.

The phosphorus contained in the trifluoride cannot be estimated by absorbing the gas in water or in an alkaline solution, since the phosphorus is not converted into a phosphite or phosphate, but into some compound which cannot be converted into a phosphate, even by boiling with dilute nitric acid.

The gas was analysed by heating a known volume in a glass vessel. Silicon fluoride is formed, and phosphorus is deposited on the glass. The volume of the former gives the amount of fluorine; the latter is dissolved in nitric acid and precipitated as magnesium ammonium phosphate. The results agree with the formula  $PF_3$ . C. H. B.

**Crystallised Hydrate of Phosphoric Acid.** By A. JOLY (*Compt. rend.*, **100**, 447—450).—Peligot has shown (*Ann. Chim. Phys.* [2], **77**, 286) that phosphoric acid,  $H_3PO_4$ , can be obtained in long chan-

nelled prisms resembling nitre by the spontaneous evaporation of a highly concentrated solution. These crystals melt at  $41.75^{\circ}$ , and dissolve in water with development of heat.

The author has observed that the mother-liquor surrounding these crystals sometimes solidifies completely during winter, but melts when the temperature rises to  $30^{\circ}$ . These easily fusible crystals dissolve in water with absorption of heat, and are a new hydrate,  $2\text{H}_3\text{PO}_4 + \text{H}_2\text{O}$ . If crystals of  $\text{H}_3\text{PO}_4$  are caused to form in a solution of the composition  $\text{H}_3\text{PO}_4 + 0.3\text{H}_2\text{O}$ , and the temperature is then reduced so that the mother-liquor also solidifies, small portions of the mixture of crystals thus obtained, when added to a concentrated solution of phosphoric acid, determine the formation of crystals of  $\text{H}_3\text{PO}_4$  or  $2\text{H}_3\text{PO}_4 + \text{H}_2\text{O}$ , according as the composition of the solution approaches more nearly to the former or the latter. Crystals of the hydrate  $2\text{H}_3\text{PO}_4 + \text{H}_2\text{O}$ , which solidify with considerable development of heat, also separate slowly from slightly more dilute solutions, in the form of prismatic lamellæ, which closely resemble the crystals of the acid  $\text{H}_3\text{PO}_4$ , but are oblique, whilst the latter are orthorhombic.

These crystals melt at about  $27^{\circ}$ ; heat of dissolution at  $+13^{\circ}$ , solid hydrate  $= +0.28$  cal.; liquid hydrate  $= +7.56$  cal. From these values it follows that the heat of fusion  $= -7.28$  cal. and (from the heat of dissolution of  $\text{H}_3\text{PO}_4$ )  $2\text{H}_3\text{PO}_4$  solid  $+ \text{H}_2\text{O}$  solid  $= 2\text{H}_3\text{PO}_4, \text{H}_2\text{O}$  solid develops  $+3.70$  cal. Combining these values with Thomsen's determinations, it is found that whilst the combination of 1 mol. phosphoric anhydride,  $\text{P}_2\text{O}_5$ , with each of the first 3 mols. of water,  $\text{H}_2\text{O}$ , develops  $9.86$  cal., combination with the fourth mol.  $\text{H}_2\text{O}$  develops only  $+3.70$  cal. The heat of dissolution of the new hydrate diminishes with the proportion of water, and is negative when this proportion is below 200  $\text{H}_2\text{O}$  to  $2\text{H}_3\text{PO}_4, \text{H}_2\text{O}$ . The value given above is for 400  $\text{H}_2\text{O}$ .

The superfused hydrate,  $2\text{H}_3\text{PO}_4, \text{H}_2\text{O}$ , crystallises in contact with the solid  $2\text{H}_3\text{AsO}_4, \text{H}_2\text{O}$ , described by Kopp, and *vice versâ*. The two hydrates are isomorphous.

Commercial phosphoric acid is a mixture of the two compounds,  $\text{H}_3\text{PO}_4$  and  $2\text{H}_3\text{PO}_4, \text{H}_2\text{O}$ .  
C. H. B.

**Action of Sulphur on Amorphous Phosphorus.** By F. ISAMBERT (*Compt. rend.*, 100, 355—356).—The author has previously found that amorphous phosphorus and sulphur combine at  $180^{\circ}$  with considerable development of heat, although the heat of formation of the phosphorus sulphide is only about  $18.4$  cal., and the tension of transformation of the amorphous phosphorus is only very feeble at this temperature (Lemôine). It seemed possible that this phenomenon might be due to some different condition of the phosphorus resulting from its mode of preparation.

Some amorphous phosphorus was prepared by heating yellow phosphorus in a sealed tube in a combustion furnace, and purifying the product by boiling with potash solution. When the amorphous phosphorus thus obtained is heated gradually to  $260^{\circ}$  with sulphur, combination takes place slowly and incompletely without any explosion.

When strongly heated the two substances combine without appreciable thermal disturbance.

It is evident that when amorphous phosphorus is concerned in a reaction, the method by which it has been prepared, or, better, its heat of formation, should be known.

C. H. B.

**Non-existence of Ammonium Hydroxide.** By D. TOMMASI (*Bull. Soc. Chim.*, **42**, 216—217; comp. Abstr., 1884, 1247).—Further proof of the difference in constitution of the aqueous solution of ammonia gas and the aqueous solutions of the hydroxides of the alkali-metals, is afforded by Bouty's determination of their relative electrical conductivity (Abstr., 1884, 1242). The solution of ammonia is a feeble conductor of electricity, but the solutions of the alkaline hydroxides are all good conductors.

W. R. D.

**Action of Boric Acid on Calcium Carbonate in the Cold.** By L. REED (*Chem. News*, **51**, 63).—When a mixture of finely powdered boric acid and calcium carbonate is made into a thick paste and allowed to dry spontaneously, the surface becomes hardened after a few days, and can only be scratched with difficulty by the finger nail. This occurs even when the proportion of the boric acid to the chalk is only 1 : 30. The hardness is only superficial, and is apparently due to the formation of a thin layer of a calcium borate. This change is greatly hindered by the presence of very small quantities of foreign substances, such as mercury iodide, ultramarine, or lead chromate.

D. A. I.

**Atomic Weight of Beryllium.** By W. N. HARTLEY (*Proc. Roy. Soc.*, **36**, 462—464).—The author quotes from his papers (*Trans.*, 1883, 316, 390) on this subject, with a view of pointing out that the spectrum of beryllium exhibits no marked analogies with the calcium, magnesium, or aluminium spectra, and, therefore, from this relationship only, it cannot be conveniently classed with any of these metals. The spectra of magnesium, zinc, and cadmium are the results of three series of harmonic vibrations with similar intervals, the fundamental vibrations of which differ in pitch; similar observations have been made in the case of copper, silver, and mercury; aluminium, indium, and thallium; and of calcium, strontium, and barium. The author believes that such series of elements present the same kind of matter in different states of condensation, consisting of similarly constituted molecules, the vibrations of which are in the same direction and at similar intervals, but with different velocities.

Beryllium cannot also be classified with scandium and yttrium, or with cerium, lanthanum, and didymium; so that it is only by first applying the method of difference, and then the method of agreement, that this element falls into the dyad series.

V. H. V.

**Solubility of Magnesium Carbonate in Carbonic Acid.** By R. ENGEL (*Compt. rend.*, **100**, 352—355 and 444—447).—The author shows that the numbers obtained by himself and Ville prove that the solubility of magnesium carbonate in water in presence of carbonic anhydride follows the law of two progressive series, as found by Schloesing in the case of barium and calcium carbonates.

The discordant results obtained by other observers are due to the fact that they employed magnesium hydrocarbonate, which behaves in presence of carbonic acid in a manner very different from that of magnesia or normal magnesium carbonate. Its maximum solubility is only attained after very prolonged treatment with carbonic anhydride in presence of water.

The author used crystallised magnesium carbonate,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ , and determined the solubility under different pressures at  $12^\circ$  and under atmospheric pressure at different temperatures. The results obtained agree well with those calculated by the formula  $x^m = Ky$ ,  $m$  being  $= 0.370$  and  $K$   $0.03814$ . The coefficient  $m$  differs very little from the coefficients for calcium carbonate ( $0.378$ ) and barium carbonate ( $0.380$ ) as determined by Schloesing. The results may be approximately expressed by the rule that the amount of magnesium carbonate dissolved by carbonic acid at constant temperature is proportional to the cube root of the pressure of the carbonic anhydride.

The results obtained at different temperatures under atmospheric pressure show that the amount of magnesium carbonate dissolved is sensibly proportional to the coefficient of solubility of carbonic anhydride at the particular temperature.

C. H. B.

**Ammonio-zinc Sulphates; Separation of an Aqueous Solution into Two Layers.** By G. ANDRÉ (*Compt. rend.*, **100**, 241—243).—When a current of ammonia gas is passed into a cooled solution of zinc sulphate in aqueous ammonia, the solution becomes opalescent; and if the passage of the gas is discontinued at this point, the liquid separates into two layers. When agitated, the two layers form an emulsion, but they rapidly separate again on standing. If the passage of the ammonia gas is continued, the bulk of the lower layer increases, and deliquescent needles separate, of the composition  $\text{ZnSO}_4 \cdot 4\text{NH}_3 + 3\text{H}_2\text{O}$ . If the lower layer is allowed to remain by itself, it usually does not crystallise, but in some cases large tabular crystals of the same composition as the needles are deposited. When the lower layer is agitated with alcohol, they do not mix, but slender needles gradually separate at the junction of the two liquids.

If a mixture of crystals and the lower liquid is gently heated at about  $20^\circ$ , the crystals dissolve with evolution of ammonia, and an oily lower layer then separates and gradually increases in volume. At  $28^\circ$  all the crystals have disappeared, and at  $36^\circ$  the liquid becomes homogeneous.

The upper layer has a sp. gr. of  $0.953$  at  $8^\circ$ , and contains ammonia  $25.69$  per cent. and zinc  $2.15$  per cent.; the lower layer has a sp. gr. of  $1.2714$  at  $8^\circ$ , and contains ammonia  $22.16$  per cent., zinc  $13.62$  per cent.

The separation into two layers can be observed with strong aqueous ammonia and an aqueous solution of zinc sulphate.

C. H. B.

**Cellular Structure of Fused Steel.** By OSMOND and WERTH (*Compt. rend.*, **100**, 450—452).—This paper contains the results of numerous experiments made at Creusot.

When thin sections of fused steel, 0.02 or 0.03 mm. in thickness, are attached to glass by means of Canada balsam, and treated with cold dilute nitric acid, the iron dissolves, leaving a residue of a nitro-derivative of a carbohydrate, and the skeleton thus obtained shows the distribution of the carbon in the original steel. It is found that fused steel has a cellular structure, the nuclei consisting of pure iron and the envelopes of a carbide of iron. These simple cellules are grouped in compound cellules, the bounding surfaces of which are soft iron free from carbon. The bounding surfaces of the compound cellules are closed polygons, and in cast steel they attain somewhat large dimensions; but they become smaller and more broken and confused in proportion as the steel has been subjected to mechanical treatment. These compound cellules are identical with what is commonly called the grain of the steel and their faces are regions of less cohesion: hence it may be said that the fracture of a bar of steel is that surface, which in the portion affected by the strain, contained the smallest proportion of carbon.

When a bar of steel is dissolved as in Weyl's method for the determination of carbon, the residue, which consists of a carbide of iron, retains the appearance and dimensions of the original bar, and it is seen that the small plates of the carbide form a network within the meshes of which the pure iron was contained. The carbide is gradually attacked by the acid.

If polished surfaces of steel are treated with strong nitric acid, the passivity of the iron limits the corrosion to a very thin layer, and the crystalline structure of the globulites of iron is well seen. The compound cellules seem to be the result of independent dendritic aggregations, which have mutually limited one another, and expelled from their lines of junction the still liquid carbide of iron.

The above results refer to steel which has cooled slowly. After tempering, the compound cellules have disappeared, and the steel is made up of simple cellules. The interspersed carbide of iron is much rarer than in the same steel after melting, and the manner in which the excess of carbon separates in Weyl's process, indicates that this fraction is uniformly diffused or dissolved in the whole mass of the metal.

Hammered steel is mainly characterised by a permanent distortion of the cellules, with elongation of the nuclei, and more or less complete fracture of the less malleable envelopes. C. H. B.

**Tungstates of Barium, Strontium, and Calcium.** By G. v. KNORRE (*Ber.*, 18, 326—328).—Of the tungstates in which the ratio of base to acid is 3 : 7 or 5 : 12, only those of the alkalis, of lithium, and some double salts have been thoroughly examined. Lotz described a barium salt,  $3\text{BaO}, 7\text{WO}_3 + 8\text{H}_2\text{O}$ , and strontium salt,  $3\text{SrO}, 7\text{WO}_3 + 8\text{H}_2\text{O}$  (*Annalen*, 91, 60); but as Scheibler has since stated (*J. pr. Chem.*, 83, 295) that homogeneous substances cannot be obtained by precipitating metallic salts with sodium paratungstate, it appeared advisable to reinvestigate the question. The author finds that homogeneous salts can be obtained by adding a hot solution of sodium paratungstate to a hot solution of barium, calcium, or strontium

chlorides or nitrates, provided that more than 3 mols. BaO, SrO, or CaO are present for every 7 mols.  $\text{WO}_3$ . If, however, excess of tungstate is employed, homogeneous substances are not obtained.

*Barium paratungstate*,  $\text{Ba}_3\text{W}_7\text{O}_{24} + 16\text{H}_2\text{O}$ , forms a granulo-crystalline powder; it loses 8 mols.  $\text{H}_2\text{O}$  when dried over sulphuric acid. It is insoluble in cold, sparingly soluble in hot water. It melts at a red heat, and on cooling forms a conglomerate of greyish-blue crystals. The *strontium* salt,  $\text{Sr}_3\text{W}_7\text{O}_{24} + 16\text{H}_2\text{O}$ , resembles the barium salt, but does not fuse at a red heat. The *calcium* salt,  $\text{Ca}_3\text{W}_7\text{O}_{24} + 18\text{H}_2\text{O}$ , closely resembles the foregoing, except that it is much more soluble in water, and therefore can be obtained in better crystals. It does not melt at a red heat.

A. J. G.

**Platinum Carbides formed at Comparatively Low Temperatures.** By A. B. GRIFFITHS (*Chem. News*, 51, 97).—In contact with carbon, platinum fuses at comparatively low temperatures, without blast. A small quantity of the carbon is taken up by the molten metal, and on cooling crystallises out as graphite.

D. A. L.

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## Mineralogical Chemistry.

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**Crystallised Gold in Prismatic Forms.** By W. P. BLAKE (*Amer. J. Sci.* [3], 28, 57—58).—Near Clancey, Jefferson Co., Montana, minute crystals of gold occur which present the novelty of a solid octahedral head, with a long divergent prismatic development of the gold on one side, giving the whole the appearance of a comet. The total length of the crystals is about one-eighth of an inch.

From Sonora, in Tuolumne Co., California, the author obtained a sample of very small, brilliant prisms of gold. Under the microscope, they are seen to be hexagonal prisms, terminated at one or both ends with a pyramid. They resemble the prismatic crystals obtained by Chester (Abstr., 1878, 938), by digesting gold amalgam in nitric acid. B. H. B.

**Ozokerite and Ceresine of Galicia.** By GRABOWSKI (*Chem. Centr.*, 1884, 285—286).—Ozokerite is found at Boryslaff and Slamslawóff, both on the northern flanks of the Carpathians. The miocene formation of this district is important on account of the numerous naphtha springs. The ozokerite occurs chiefly in thin layers and small pockets mixed with earthy matters. The best earth-wax has a yellowish or greenish colour, and is easily compressed between the fingers. Inferior varieties are soft from the presence of too much naphtha, or hard, requiring too high a temperature for fusion. In obtaining paraffin from ozokerite the products are: benzene 2—8 per cent.; naphtha, 15—20; paraffin, 36—50; heavy oil, 15—20; coke, 10—20 per cent. Only the best varieties of ozokerite are used in the



production of ceresine, various methods of purification being employed which are mostly kept secret. J. T.

**Origin of Bitumens.** By S. F. PECKHAM (*Amer. J. Sci.* [3], **28**, 105—117).—In reviewing the speculations regarding the origin of bitumens (asphalt, naphtha, petroleum, &c.) pursued during the last half century, the author deals with the views of those who regard bitumen as a product of chemical action, as indigenous to the rocks in which it is found, or as a distillate produced by natural causes. He is, on the whole, inclined to regard bitumens as distillates from animal or vegetable remains. Whichever hypothesis is chosen, the modifying fact must be accepted that there are four kinds of bitumen:—1. Those bitumens that form asphalt and do not contain paraffin. 2. Those bitumens that do not form asphalt and contain paraffin. 3. Those bitumens that form asphalt and contain paraffin. 4. Solid bitumens that were originally solid when cold or at ordinary temperatures. In conclusion, the author argues that if these substances were the result of a purely chemical process, we should not expect to find palæozoic petroleum of a composition corresponding with the simple animal and vegetable organisms that flourished at that period, and tertiary petroleum containing nitrogen, unstable and corresponding with the decomposition-products of more highly organised beings; but we should expect to find a general uniformity in the character of the substance, wherever found, all over the earth. On the other hand, if petroleum is the product of metamorphism, its generation is co-existent only with that of metamorphic action. If we accept this hypothesis, the generation of petroleum must be considered as practically ended. B. H. B.

**Cassiterite from Irish Creek, Rockbridge Co., Virginia.** By W. G. BROWN (*Amer. Chem. J.*, **6**, 185—187).—This mineral is found in this locality in loose crystals and fragments on the surface, and in veins in places. The tin-bearing veins occur in a coarse-grained, much decomposed granite or gneiss. The cassiterite is associated with quartz and wolframite and a light-coloured mica almost invariably accompanies it; a small quantity of auriferous mispickel has also been observed. Some of the crystals of cassiterite have been examined; in one case the forms  $P$ ,  $\infty P$ ,  $\infty P\infty$ ,  $P\infty$  were observed; in another case  $P$ ,  $\infty P$ ,  $\infty P\infty$ ,  $\infty P2$ ,  $P\infty$ ,  $0P$ . The angle between  $P$ ,  $0P$  was found to be  $136^\circ 10'$ . Twinned crystals are common, the twinning plane being  $P\infty$ . The majority of the crystals are striated on  $\infty P$  parallel to the edge  $\infty P$ ,  $\infty P\infty$ . There are also striations on  $\infty P$  parallel to the edge  $\infty P$ ,  $P\infty$ . The following is a complete analysis of the cassiterite:—

SnO <sub>2</sub> .	SiO <sub>2</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Loss on ignition.	Total.
94·895	0·760	0·237	3·418	0·244	0·27	0·385	99·966
P. P. B.							

**Herderite.** By F. A. GENTH (*Chem. News*, **51**, 86—88).—Owing to the uncertainty attached to the composition of herderite, and to the doubt as to the identity of the Ehrenfriedersdorf, Saxony, and Stone-

ham, Maine specimens, the author has made careful analyses of the latter with the following results:—

P <sub>2</sub> O <sub>5</sub> .	BeO.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	Loss.	F.	Total, less O for F.
43·43	15·04	0·20	0·15	0·11	33·65	0·61	8·93	= 98·36

These agree with the figures given by Mackintosh (Abstr., 1884, 827, and this vol., p. 359), but not with those obtained by Winckler (Abstr., 1884, 1102). The author's fluorine determination is probably too low. The mineral consists essentially of anhydrous calcium, beryllium phosphate and fluoride. The alumina is probably due to admixture with traces of mica and albite. After exposing the very faulty nature of Winckler's methods of analysis, the author concludes that there can be little doubt as to the chemical identity of the Saxon and American specimens of herderite. The author points out that beryllia is soluble in a boiling solution of ammonium chloride.

D. A. L.

**Specimens of Nickel-ore from Nevada.** By S. B. NEWBERRY (*Amer. J. Sci.* [3], **28**, 122).—The analysis of these samples of nickel-ore from Churchill Co., Nevada, gave the following results:—

NiO.	As <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.
33·71	36·44	24·77

The remaining 5 per cent. represents small quantities of iron, copper, and insoluble residue, with traces of cobalt. From the purity and richness of the ore there can be little doubt that if future developments should bear out the present indications, the mines of Nevada will eventually become a prominent source of the world's supply of nickel.

B. H. B.

**Vanadinite in Arizona.** By F. H. BLAKE (*Amer. J. Sci.* [3], **28**, 145).—This rare mineral has been found at the Black Prince Mine, Pinal Co., Arizona, in brilliant red and yellow hexagonal crystals. Qualitative tests show the presence of vanadium, chlorine, and lead. The simple hexagonal prism predominates as the crystalline form, although in some groups of crystals, the combination of the two prisms,  $\infty P$  and  $\infty P_2$ , with the basal edges replaced by minute planes of the pyramid of the first series, is found.

B. H. B.

**Monazitic Sands of Caravellas, Province of Bahia, Brazil.** By H. GORCEIX (*Compt. rend.*, **100**, 356—358).—At Caravellas, in Bahia, there are banks of sand consisting largely of brilliant yellow grains of monazite mixed with some titaniferous magnetite. After removal of the magnetite by means of a magnet, the sand has the density 5·1 and the following composition:—(SiO<sub>2</sub> 3·4, ZrO<sub>2</sub> 6·3) 9·7; CaO, 1·1; P<sub>2</sub>O<sub>5</sub>, 25·7; CeO, 28·0; DiO + LaO? 35·8 = 100·3. The silica and zirconia are insoluble in sulphuric acid; the soluble portion has the percentage composition P<sub>2</sub>O<sub>5</sub>, 28·7; CeO, 31·3; DiO + LaO?, 39·9 = 99·9, which corresponds with the formula



The Caravellas sand consists of titaniferous magnetite, zircon, and

monazite, the latter differing from previously known specimens by its richness in didymium.

C. H. B.

**Analysis of Chrysotile: Fibrous Silica from Serpentine.** By A. TERREIL (*Compt. rend.*, 100, 251—252).—The chrysotile examined was a greyish-white asbestiform specimen from Canada; density = 2.56. After drying at 100°, it had the composition  $\text{SiO}_2$ , 37.10;  $\text{MgO}$ , 39.94;  $\text{FeO}$ , 5.73;  $\text{Al}_2\text{O}_3$ , traces;  $\text{H}_2\text{O}$ , 16.85 = 99.62. These numbers agree fairly well with the formula  $6(\text{SiO}_2 + 2\text{MgO}), \text{FeO}, \text{SiO}_2 + 10\text{H}_2\text{O}$ . This silicate is infusible before the blowpipe. Boiling acids dissolve out the magnesia and ferrous oxide; the residual silica is brilliantly white and retains the fibrous form of the mineral. After drying at 100°, it retains 9.8 per cent. of water. After heating to redness, the fibrous silica retains the flexibility of silk. It dissolves in boiling concentrated potash solution, and the solution acts on polarised light in the same manner as the original silicate.

It is well known that serpentines are decomposed by boiling acids, especially by strong sulphuric acid. This decomposition takes place slowly with massive specimens, much more rapidly with fibrous or lamellar serpentines, and almost instantly in the case of specimens similar to Canadian chrysotile. The silica which is liberated by the decomposition of these magnesian silicates is not gelatinous, but has the properties described above.

C. H. B.

**Occurrence of Alkalis in Beryl.** By S. L. PENFIELD (*Amer. J. Sci.* [3], 28, 25—32).—The author's attention was first called to the occurrence of alkalis in beryl, by the detection of caesium in the qualitative analysis of an unknown silicate from Norway, Maine, and after finding alkalis in one beryl, it seemed to be of interest to examine others from various localities. The result has been to show that, as far as examined, they always contain alkalis, although sometimes only in small quantities. Sodium and lithium were always present, caesium occasionally, whilst potassium and rubidium were never detected. To prove, if possible, that the alkalis replace beryllium, a series of analyses were made, the results of which are given. The varieties analysed are:—1. From Hebron, Maine. The material was taken from a fragment of a very much cracked, colourless crystal embedded in lepidolite. It is interesting as showing that the beryl contains much more caesium than the lepidolite. 2. From Norway, Maine. 3. From Branchville, Connecticut. 4. From Amelia Court House, Virginia. 5. From Royalston, Mass. 6. From Stoneham, Maine. 7. From Aduntschilon, Siberia.

	1.	2.	3.	4.	5.	6.	7.
$\text{SiO}_2$ ...	62.10	64.29	64.74	65.13	65.14	65.20	66.17
$\text{Al}_2\text{O}_3$ ...	18.92	18.89	20.13	20.80	19.83	20.25	20.39
$\text{Fe}_2\text{O}_3$ ...	—	—	—	—	0.44	—	—
$\text{FeO}$ ...	0.49	0.48	0.54	0.49	0.78	0.66	0.69
$\text{BeO}$ ...	10.35	10.54	10.26	11.03	11.32	11.46	11.50
$\text{Cs}_2\text{O}$ ...	2.92	1.66	—	—	—	—	—
$\text{Na}_2\text{O}$ ...	1.82	1.39	1.45	0.46	0.51	0.49	0.24
$\text{Li}_2\text{O}$ ...	1.17	0.84	0.72	0.13	0.05	trace	trace

	1.	2.	3.	4.	5.	6.	7.
Ignition	2.33	2.44	2.69	2.19	2.04	2.08	1.14
CaO ...	0.35	—	—	—	—	—	—
MgO...	—	—	—	—	0.34	—	—
Total...	100.45	100.53	100.53	100.23	100.45	100.14	100.13
Density.	—	2.744	2.732	2.685	2.711	2.708	2.676

From these results the author concludes that alkalis are always present in beryl, undoubtedly replacing the beryllium, that water is also present and cannot be disregarded in the formula, and that the formula  $\text{Al}_4\text{Be}_3\text{H}_2\text{Si}_{11}\text{O}_{34}$  is the one agreeing best with the analyses.

B. H. B.

**Mineralogical Notes.** By F. W. CLARKE and T. M. CHATARD (*Amer. J. Sci.* [3], **28**, 20—25).—The authors give the following analyses executed by them in the laboratory of the U.S. Geological Survey.

1. *Jade and Pectolite*.—Among the Eskimo jade implements collected at Point Barrow, Alaska, were two varieties of a material apparently jade, one pale apple-green (I); the other (II) dark green:—

	H <sub>2</sub> O.	SiO <sub>2</sub> .	FeO.	CaO.	MgO.	Al <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	Total.
I.	4.09	53.94	trace	32.21	1.43	0.58	8.57	100.82
II.	1.41	57.01	6.95	12.75	21.36	0.42	—	99.90

The dark-green mineral is obviously jade or nephrite; while the light-green mineral agrees in composition with pectolite.

2. *Saussurite*.—From Pitt River Ferry, Shasta Co., California. Density 3.148.

Loss on ignition.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	FeO.	Na <sub>2</sub> O.	MgO.	Total.
2.42	42.79	29.43	18.13	3.65	2.51	1.40	100.33

3. *Allanite*, from Sprague's granite quarry, Topsham, Maine.

Loss on ignition.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CeO,LaO,DiO.	CaO.	MgO.	Total.
4.13	34.97	12.83	18.11	2.82	17.26	7.21	1.40	98.73.

4. *Damourite*, from Stoneham, Maine.

	Loss on ignition.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.
A.	4.48	45.19	33.32	4.25	0.58	trace	0.36
B.	4.78	45.34	33.96	3.96	0.51	0.22	0.10

	Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.
A.	1.57	11.06	100.81
B.	1.49	10.73	101.09

A. Sub-fibrous, compact, light greyish-green. B. Broadly foliated micaceous, light greyish-green.

5. *Margarite*.—A. From Soapstone Hill, near Gainesville. Density 3.0. H. = 3.5. B. An altered crystal of corundum from Iredell Co., North Carolina.

	Loss on ignition.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	Total.
A.	4·88	31·72	50·03	trace	11·57	0·12	2·26	100·58
B.	5·68	31·15	49·51	—	11·13	0·45	2·74	100·66

6. *Cimolite*.—Several specimens of tourmaline, from Maine, are encrusted with a pink earthy alteration-product, the analysis of which gave results approaching those required by the formula  $\text{AlH}_3(\text{SiO}_3)_3$ .

H <sub>2</sub> O.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	MgO.	Total.
9·53	70·06	17·19	2·28	0·80	99·86

7. *Halloysite*, from the Detroit Copper Mine, near Mono Lake, California.

H <sub>2</sub> O.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Total.
18·95	42·91	38·13	99·99

8. *Prochlorite*, from Foundry Run, Georgetown, District of Columbia.

H <sub>2</sub> O.	SiO <sub>2</sub> .	MgO.	Al <sub>2</sub> O <sub>3</sub> .	FeO.	Na <sub>2</sub> O.	Total.
14·43	25·45	15·04	17·88	24·98	0·67	98·45

9. *Halotrichite*, from the Gila River, near Silver City, New Mexico, where there is a deposit of this mineral covering 2,000 acres.

H <sub>2</sub> O.	SO <sub>3</sub> .	FeO.	Al <sub>2</sub> O <sub>3</sub> .	Insoluble.	Total.
40·62	37·19	13·59	7·27	0·50	99·17

10. *Alunogen*.—Associated with the halotrichite are great quantities of alunogen.

H <sub>2</sub> O.	SO <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Insoluble.	Total.
42·56	34·43	15·52	7·62	100·13

The following minerals from new localities have also come under the notice of the authors:—*Vivianite*, from Washington, District of Columbia; *hyalite*, from Foster's mica mine, near Jefferson, North Carolina; *beryl*, from Gilmore's mica mine, in Montgomery Co., Maryland; and *cassiterite*, from the Brewer gold mine, South Carolina.

B. H. B.

**Paramorphosis of Pyroxene to Hornblende in Rocks.** By G. H. WILLIAMS (*Amer. J. Sci.* [3], 28, 259—268).—It has long been recognised that pyroxene and hornblende are two different crystallographic forms of essentially the same molecule, of which the former is most stable at high, the latter at ordinary temperatures. Several cases, recently noted by the author, are described, where a direct change of pyroxene to compact hornblende is admirably exhibited in every stage. In a rock of the Cortlandt Series, on the northern shore of Montrose Point, south of Peekskill, on the Hudson River, this process of change is especially apparent. The ground-mass of the rock is composed almost entirely of rounded grains of compact brown hornblende. Interspersed among these are frequent hypersthene grains of precisely the same shape, and in every possible stage of transition to hornblende. Microscopic sections of

gabbros, from Eagle Harbour, Ashland Co., Wisconsin, show the undoubted change of the pyroxene into single individuals of compact brown hornblende. The so-called black granite, from Addison, Maine, seems to have originally been an augite-plagioclase rock containing biotite. The augite, however, is undergoing paramorphosis to corresponding crystals of compact green hornblende.

In suggesting pressure as a possible cause of the change, by molecular rearrangement of pyroxene to amphibole, the author does not desire to claim that it is the only cause of the paramorphosis, or, indeed, that it is ever absolutely necessary. The range of observations is as yet too small to allow of any generalisation.

B. H. B.

**Fulgurite, from Mt. Thielson, Oregon.** By J. S. DILLER (*Amer. J. Sci.* [3], 28, 252—258).—Among the specimens collected upon the summit of Mt. Thielson, by E. E. Hayden, of the U.S. Geological Survey, are several fulgurites that had been formed by the fusion of an interesting basalt, in which, instead of augite, there is a hypersthene associated with the olivine. The fulgurite occurs in the form of a superficial coating and as lightning tubes. It is unevenly distributed over a considerable surface in patches of drops and bubbles of glass. The glass is translucent, and has a greenish-brown colour. It is rather tough, strongly lustrous, has a density of 2·5, and a hardness a little below that of ordinary glass. Thin splinters readily fuse without intumescence. The ground-mass of the rock fuses to a dark glass much less readily than the fulgurite. Small fragments of the fulgurite when heated become strongly magnetic. It appears to be entirely insoluble in strong acids. The entire absence of all crystallites and microliths may be used as a means of distinguishing fulgurites from other natural glasses. The microscope reveals the fact that the fulgurite was formed chiefly by the fusion of the ground-mass. This is also clearly shown by the following analyses:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.
Fulgurite . . . .	55·04	28·99	7·86	5·85	—	—
Ground-mass .	55·85	22·95	4·59	8·41	3·08	2·67

	Na <sub>2</sub> O.	Ignition.	Total.
Fulgurite . . . . .	—	1·11	98·85
Ground-mass. . . . .	2·16	0·52	100·23

B. H. B.

**Meteoric Iron from Wichita Co., Texas.** By J. W. MALLET (*Amer. J. Sci.* [3], 28, 285—288).—The meteorite is now preserved in the University of Texas. It has an irregular, pear-like shape, with tolerably smooth general surface. There is no well-defined crust, but merely a thin film of oxide on the surface. The maximum length of the specimen in its original state was 595 mm.; maximum breadth, 305 mm.; maximum thickness, 223 mm.; and weight, 160 kilos. Most of the iron in the interior was compact, tolerably soft, and malleable. Nodules of troilite occasionally occurred. Schreibersite is not very abundant. The average density of the whole mass

was found to be 7·841. A polished surface when etched with nitric acid clearly showed Widmannstättian figures. The analysis of an average sample of the mass gave the following results:—

Fe.	Ni.	Co.	Mn.	Cu.	Sn.	P.	S.
90·769	8·342	0·265	trace	0·018	0·004	0·141	0·016
Graphitic carbon.			SiO <sub>2</sub> and Fe <sub>2</sub> O <sub>3</sub> .		Total.		
0·190			0·132		99·877		

The most interesting point about this specimen is the probability of its forming a separate portion of the same meteoric fall, from which was derived the large iron meteorite, weighing 1,635 lbs., described by Gibbs, in 1814, and now in the collection of Yale College. B. H. B.

**New Meteorite.** By I. R. EASTMAN (*Amer. J. Sci.* [3], 28, 299—300).—At Grand Rapids, Michigan, a pear-shaped meteoric mass was discovered in May, 1883. It was 14 inches long, 9·6 inches in diameter at the thickest part, and weighed 114 lbs. A preliminary analysis of 24 grains gave the following results:—

Fe.	Ni.	Co.	Insoluble residue.
94·543	3·815	0·396	0·118

The entire specimen is now in the Smithsonian Institution for examination. B. H. B.

**Mineral Water of Acquarossa.** By G. BERTONI (*Gazzetta*, 14, 232—233).—The Acquarossa springs are situated on the Lukmanier Pass, in the Canton Ticino. The following results, grams per 10 kilograms, were obtained on analysis:—

Ferrous bicarbonate .....	0·3469
Manganese bicarbonate .....	0·0193
Calcium bicarbonate .....	6·5967
Calcium arsenate .....	0·0024
Magnesium borate .....	0·0254
Calcium sulphate.....	11·5172
Potassium sulphate.....	0·4179
Sodium sulphate.....	0·884
Magnesium sulphate .....	5·0805
Lithium chloride.....	0·0467
Magnesium chloride .....	0·0165
Alumina .....	0·0485
Silica.....	0·3518
Carbonic anhydride.....	3·7828
Nitrogen .....	0·1418
Oxygen.....	0·0233

There was also present 0·0065 gram ochreous suspended matter, which contained a much larger proportion of arsenic than the celebrated sediment of Levico, so that its collection might be rendered profitable for its utilisation for some skin diseases. V. H. V.

## Organic Chemistry.

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**Separation of Butylenes.** By M. CHECHOUKOFF (*J. Russ. Chem. Soc.*, 1885, 56).—In order to separate the butylenes obtained by Puchot's method (Abstr., 1884, 166), the gases are absorbed by strong hydriodic acid, and the product containing the iodides is poured into water; if the water is cold, the tertiary iodide is converted to trimethylcarbinol, whilst if it is boiling, isobutylene is produced, the secondary butyl iodide remaining unchanged in both cases.

A. T.

**Diallyl.** By A. SABANIEFF (*J. Russ. Chem. Soc.*, 1885, 35).—On treating diallyl (boiling at  $59^{\circ}$ ), prepared by the action of sodium on allyl iodide, with bromine, a crystalline mass is obtained, melting at  $46^{\circ}$ ; this is a mixture of two different kinds of crystals, the one large quadrilateral prisms, melting at  $64$ – $65^{\circ}$ , the other small stellate or nodular concretions, melting at  $54$ – $56^{\circ}$ ; both have the composition  $C_6H_{10}Br_4$ . Hence the author concludes that diallyl must be a mixture of two isomerides, diallyl,  $CH_2:CH.CH_2.CH_2.CH:CH_2$ , and dipropenyl,  $CH_3.(CH)_4.CH_3$ , such a view being supported by its products of oxidation (Sorokine, Abstr., 1878, 962, and 1880, 370).

A. T.

**Trimethylene Iodide.** By W. H. PERKIN, JUN. (*Ber.*, 18, 221).—When trimethylene bromide is heated on a water-bath with twice the theoretical amount of potassium iodide and some alcohol, an almost quantitative yield of trimethylene iodide,  $C_3H_6I_2$ , is obtained. The product of the reaction is treated with water and agitated with ether; the ethereal solution is washed with water, shaken with mercury, and dried. The ether is then distilled off, and the residue fractioned under diminished pressure. Under atmospheric pressure trimethylene iodide boils at  $215$ – $220^{\circ}$ , with slight decomposition; it does not solidify at  $-10^{\circ}$ . Its sp. gr. is 2.59617 at  $4^{\circ}$ , 2.57612 at  $15^{\circ}$ , and 2.56144 at  $25^{\circ}$ , compared in each case with water at the same temperature.

A. K. M.

**Decomposition of Potassium Cyanide.** By J. F. WILKES (*Chem. News*, 51, 45–46).—When carefully purified air is passed over pure potassium cyanide moistened with water, at a temperature of from  $12^{\circ}$  to  $15^{\circ}$ , hydrocyanic acid is present in the issuing air. When the amount of moisture is small, 1 c.c. of water to 1 gram of cyanide, the evolution of hydrocyanic acid is likewise small, and the amount evolved is not increased by the admixture of calcium carbonate, gypsum, or barium sulphate; an increase is, however, observed when anhydrous calcium sulphate is mixed with the slightly moistened cyanide (the mixture employed by entomologists in their bottles for killing insects), but this increase is not observed when excess of water (3–5 c.c.) is added to the mixture. Porous partially anhydrous calcium chloride and anhydrous sodium carbonate behave in a manner similar to the anhydrous calcium sulphate, and it seems that the



increased activity is due to the dehydrating power of these substances. With the increased rapidity of decomposition, the mixture becomes discoloured, and potassium hydroxide can be detected in it after two or three days' action. Hydrocyanic acid is not evolved from the mixture when both the cyanide and the sulphate are dry. D. A. L.

**Green Ferrocyanides or Glaucoferrocyanides.** By A. ÉTARD and G. BÉMONT (*Compt. rend.*, **100**, 275—277).—Ferrocyanides of the type  $R_4FeCy_4 \cdot 2NH_4Cl$  (this vol., p. 365), when heated with water at  $100^\circ$  for several days, slowly decompose with liberation of hydrocyanic acid and ammonium cyanide, and formation of a soluble chloride and a green crystalline salt insoluble in all reagents. For these insoluble salts the author proposes the name *glaucoferrocyanides*.

The salt obtained by the prolonged heating of a solution of equal parts of potassium ferrocyanide and ammonium chloride has the formula  $C_{20}N_{25}H_{24}Fe_6K_2O$ . It is Williamson's salt modified by the action of the ammonium chloride. When boiled with potash, half the iron is precipitated, whilst the other half is converted into potassium ferrocyanide, and ammonia is given off. The salt may therefore be represented by the formula  $(FeCy_6Fe)_3K_2(NH_4)_5(CN,H)_2 + H_2O$ .

When this compound is heated in a vacuum at  $440^\circ$ , it loses 25.2 per cent. of water, hydrocyanic acid, hydrogen, and ammonium cyanide, and yields an insoluble chamois-coloured compound, which oxidises when exposed to air, and has the formula  $2Fe_2FeCy_6 \cdot 2KCN$ . When treated with excess of bromine-water, this pyro-derivative yields a blue compound of the composition  $Fe_2(FeCy_6)_2 + 8H_2O$ . The same change is produced by moist air.

When the glaucoferrocyanide is treated with bromine-water in the cold, it yields a compound which resembles Turnbull's blue, and has the formula  $C_{11}N_{14}H_7Fe_4 + 4H_2O$ . C. H. B.

**Oxidations by Hydrogen Peroxide.** By B. RADZISZEWSKI (*Ber.*, **18**, 355—356).—Nitriles are rapidly converted into amides by hydrogen peroxide, in accordance with the equation  $R.CN + 2H_2O_2 = R.CONH_2 + O_2 + H_2O$ . The reaction occurs very readily in alkaline solution, and at a temperature of about  $40^\circ$ . When cyanogen is dissolved in a 3 per cent. solution of hydrogen peroxide, oxygen is evolved after a few minutes, and on addition of a drop of potash, oxamide separates in long needles. The reaction is unaccompanied by the formation of bye-products, and can be used as a lecture experiment. A. J. G.

**Continuous Etherification.** By L. M. NORTON and C. O. PRESCOTT (*Amer. Chem. J.*, **6**, 241—246).—Little further has been made known on this subject since Williamson's researches. The conversion of ethyl alcohol into its ether commences at  $115$ — $120^\circ$ , when the yield amounts to 4.2 per cent. of the theoretical; it is most complete at  $140$ — $145^\circ$ , when the yield is 47—52 per cent., and is still considerable at  $160^\circ$  (48 per cent.): but above this temperature sulphurous acid is evolved, and the sulphuric acid is soon destroyed. Propyl alcohol is similarly converted into its ether at  $135^\circ$ ; the yield is very

good. Neither isobutyl alcohol nor isoamyl alcohol can be converted into their ethers by this method, the acid is destroyed, tars are formed, and the alcohols then distil over unchanged.

A mixture of equal molecular proportions of methyl and ethyl alcohols at  $140^{\circ}$ , yields methyl ether, ethyl ether, and, in largest quantity, methyl ethyl ether. In similar manner, ethyl propyl ether may be obtained from a mixture of the alcohols; but neither ethyl isobutyl ether nor methyl isoamyl ether could be so prepared, although the latter is stated by Williamson to be formed in this way; Guthrie also was unable to obtain ethyl isoamyl ether (*Annalen*, **105**, 37). The author concludes that the process of continuous etherification can only be applied to the formation of the simple and mixed ethers from alcohols containing not more than 3 atoms of carbon. H. B.

**Isopropylallyl Dimethyl Carbinol and its Derivatives.** By N. KONONOWITZ (*J. pr. Chem.* [2], **30**, 399—410).—The occurrence of isopropylallyl dimethyl carbinol as a bye-product in the preparation of allyl dimethyl carbinol has been observed by Dieff (Abstr., 1883, 1076) and Putochin (*Ber.*, **16**, 2285). The methylic ether,  $C_9H_{17}.OMe$ , prepared by the action of methyl iodide on the sodium compound of this alcohol, is a colourless liquid, miscible with alcohol and ether, and boiling at  $169$ — $172^{\circ}$ ; its sp. gr. at  $21.6^{\circ}$  is  $0.8027$ , compared with water at  $4^{\circ}$ . Molecular refraction  $77.01$ . The ether absorbs 2 atoms of bromine, forming the dibromide  $C_9H_{17}Br_2.OMe$ . On oxidation with chromic mixture, isobutyric and acetic acids are formed, but on oxidation with potassium permanganate, acetic, isobutyric, oxalic, and methhydroxyvaleric acids,  $C_6H_{12}O_3$ , are obtained. The latter acid is a syrupy liquid, yielding amorphous calcium and barium salts, which are soluble in alcohol and water. Isopropylallyl dimethyl carbinol splits up into acetic and isobutyric acids on oxidation, hence it probably has the constitution  $CHMe_2.CH:CH.CH_2.CMe_2.OH$ .

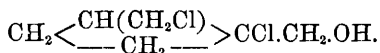
W. C. W.

**Action of Allyl Iodide and Zinc on Epichlorhydrin.** By M. LOPATKIN (*J. pr. Chem.* [2], **30**, 389—399).—A chlorinated alcohol,  $CH_2Cl.CH(OH).CH_2.C_3H_5$  or  $CH_2Cl.CH(C_3H_5).CH_2.OH$ , is formed by the action of zinc on a mixture of allyl iodide and epichlorhydrin. The alcohol is a mobile liquid, boiling at  $183$ — $187^{\circ}$ . It is of a pale yellow colour, but soon darkens on exposure to the light. It is miscible with ether and alcohol, and its sp. gr. is  $1.030$  at  $20^{\circ}$ , compared with water at  $4^{\circ}$ . The alcohol unites directly with 2 atoms of bromine. The acetate,  $C_5H_{10}AcClO$ , is a colourless liquid boiling at  $203$ — $207^{\circ}$ . The molecular refraction of the alcohol is  $R_A = 55.5$ , and of the acetate  $71.10$ . On oxidation with chromic mixture, the alcohol yields chlorohydroxyvaleric acid,  $C_5H_9ClO_3$ . The barium salt contains 8 mols.  $H_2O$ , and is freely soluble in water and alcohol. The sodium salt crystallises with 1 mol.  $H_2O$ , and is also freely soluble in alcohol and water.

W. C. W.

**Action of Zinc Ethyl on  $\alpha$ - $\gamma$ -Dichlorocrotonaldehyde.** By K. NATTERER (*Monatsh. Chem.*, **5**, 567—588).—The product of this reaction, when treated with dilute sulphuric acid, yields an alcohol of the formula  $C_6H_{10}Cl_2O$ ; this forms a clear thick liquid of peculiar faint

odour, boils at 115—119° under 20 mm. pressure, and is nearly insoluble in water. It behaves as a saturated compound, and seems to have the constitution



The acetate,  $\text{C}_6\text{H}_9\text{Cl}_2\text{O}.\text{Ac}$ , is prepared by the action of acetic anhydride on the alcohol; it forms a colourless, mobile liquid of agreeable fruity odour, and boils at 122—123°; when boiled with baryta-water, not only the acetyl-group, but also the greater part of the chlorine is removed. By the action of silver acetate on the acetate, one only of the chlorine-atoms is removed, and a diacetate,  $\text{C}_6\text{H}_9\text{Cl}(\text{OAc})_2$ , formed; this is a colourless liquid heavier than water, and boils at about 140° under 20 mm. pressure. By the action of iron and acetic acid on the alcohol, small quantities of ethyl, butyl, and crotonyl alcohols were formed, together with a considerable quantity of an alcohol,  $\text{C}_6\text{H}_{10}\text{Cl}.\text{OH}$ . This, like the dichlorinated derivative, acts as a saturated compound; it is a colourless, mobile liquid, boils at 165—168°, is heavier than and only sparingly soluble in water. The chlorine-atom could not be removed by boiling with baryta-water, nor by the action of sodium amalgam.

The *chloride*,  $\text{C}_6\text{H}_9\text{Cl}_3$ , formed by the action of phosphoric chloride on the alcohol,  $\text{C}_6\text{H}_9\text{Cl}_2.\text{OH}$ , is a mobile colourless liquid; it boils at about 100° under 20 mm. pressure.

By the action of bromine on the alcohol  $\text{C}_6\text{H}_{10}\text{Cl}_2\text{O}$ , a monobrominated derivative,  $\text{C}_6\text{H}_9\text{Cl}_2\text{Br}.\text{OH}$ , is formed; it boils at 160—170° under 20 mm. pressure. Oxidation experiments threw no particular light on the constitution of the dichlor-alcohol.

A. J. G.

**Glycol and Glycol Monochlorhydrin.** By G. BOUCHARDAT (*Compt. rend.*, 100, 452—453, and 453—454).—Glycol is most readily obtained in a state of purity by Zeller and Hüfner's method, that is, by boiling ethylene bromide with potassium carbonate solution. The pure product boils at 197.5°, and solidifies and melts at —11.5°, but shows great tendency to remain in superfusion. If it is cooled to —20° it may remain more than six hours without crystallising, but if it is withdrawn from the freezing mixture, and crystals of glycol are introduced, the glycol slowly separates in somewhat bulky maced crystals with brilliant faces, apparently monoclinic or triclinic. The presence of water or diethylenic alcohol lowers the freezing point very considerably.

The main inconvenience of the above method of preparing glycol is that about one-fourth of the ethylene bromide is converted into brom-ethylene. The latter may be converted into bromethylene bromide, which boils at 187° and melts at —26°.

In order to prepare glycol monochlorhydrin, crude glycol, containing some water, is saturated with hydrogen chloride, and the mixture heated in sealed tubes. When the product is distilled, it yields small quantities of ethylene chloride and hydrochloric acid, a fraction boiling at 106—107°, equal in bulk to about half the crude product, and a fraction boiling at 128°, equal to about one quarter of

the product. The same products are obtained when the residue is treated with a further quantity of hydrogen chloride.

The fraction boiling at  $106^{\circ}$  consists of a constant mixture of glycol monochlorhydrin, hydrochloric acid and water, in proportions approximating to the formula  $2C_2H_5ClO + HCl + 8H_2O$ . This mixture may be used instead of the pure chlorhydrin in many reactions. Its sp. gr. at  $0^{\circ}$  is 1.1926, that of the pure chlorhydrin being 1.2233. If the mixture is exactly neutralised with potash and the liquid distilled, pure glycol monochlorhydrin is obtained. Neither the pure product nor the mixture solidifies at  $-55^{\circ}$ , but a mixture of 1 mol. glycol monochlorhydrin with 4 mols. of water begins to solidify at  $-11^{\circ}$ , and is completely solid at  $-17^{\circ}$ . Mixtures of the chlorhydrin and water in other proportions do not solidify completely. Bromine is without action on the chlorhydrin or on the acid mixture in the cold, but decomposition takes place slowly on boiling, with formation of dibrom-acetic acid (boiling at  $135^{\circ}$  and melting at  $43-48^{\circ}$ ) and ethylene bromide, together with small quantities of bromal, carbon tetrabromide, and bromoform.

C. H. B.

**Specific Gravity, Boiling Point, and Vapour-tension of Aqueous Solutions of Glycerol.** By G. T. GERLACH (*Chem. Centr.*, 1884, 884—886; from *Chem. Ind.*, 7, 277—287), Köhn.—A very full table is given, showing the sp. gr. at  $15^{\circ}$  and at  $20^{\circ}$ , and the boiling points and the vapour-tensions at  $100^{\circ}$ , of aqueous solutions containing from 10 to 99 per cent. of glycerol.

The apparatus by means of which the vapour-tensions were determined is a modified Geissler's alcohol vaporimeter.

J. T.

**Composition of Maple Sugars and Syrups.** By H. W. WILEY (*Chem. News*, 51, 88—90).—All the sugar present in maple sap is pure sucrose, but as the sap is always evaporated in open pans, maple sugars and syrups contain invert sugar. Numerous analyses show that genuine maple sugar contains per cent. about 82 to 87 sucrose, 0.8 to 0.5 invert sugar, 8.0 to 10.75 water, and 1 to 1.25 ash; whilst genuine maple syrup may contain, per cent., about 39 to 64.5 sucrose, 0.25 to 1.75 (or even more in old samples) invert sugar, between 30 and 40 water, and 0.5 to 1.0 ash. Maple sucrose does not differ chemically from other sucroses. As maple sugars and syrups are of higher value, they are frequently adulterated with cane- and beet-sugar, or even with glucose, and now even an artificial maple flavour and odour is extracted from hickory bark. The sap from the butternut tree (*J. cinerea*), taken in spring, is scarcely inferior to maple sap.

D. A. L.

**Action of the Diastase of Malt on Crude Starch.** By L. BRASSE (*Compt. rend.*, 100, 454—456).—Previous experiments have failed to show that amylase has any action on natural or crude starch, that is, starch which has not been cooked or converted into starch-paste, but the author finds that the product extracted from sprouted barley, or from leaves, by Dubrunfaut's method, exerts a digestive action on crude starch, provided the extraction has been made in the cold and with the greatest possible rapidity in order to avoid alteration of the diastase.

This diastase partly converts crude starch into glucose, the granules being corroded as in germination. The most favourable temperature is about  $42^{\circ}$ , and the maximum of conversion is attained at the end of one or two days, according to the conditions. The proportion of glucose remains stationary, even if more diastase is added, provided the volume of the liquid is not altered, but if the liquid is diluted, a further quantity of glucose is formed until a second maximum is reached. No dextrin is formed.

No glucose is formed at  $50-57^{\circ}$ , and prolonged digestion at this temperature partially destroys the properties of the diastase. Prolonged contact with alcohol of  $63^{\circ}$  has the same effect on the diastase. Commercial diastases have no effect on crude starch, probably because they have undergone alteration in the process of extraction.

C. H. B.

**Optical Inactivity of Cellulose.** By A. BÉCHAMP (*Compt. rend.*, 100, 279—282, and 368—370).—A continuation of the controversy with Levallois. The author finds that the ammonio-copper solution prepared by Peligot's method, has a distinct rotatory power, and is sometimes dextrogyrate, sometimes lævogyrate. The amount of rotation varies with the concentration of the solution, but is not proportional to the amount of copper which the liquid contains. This phenomenon is possibly connected with the colloidal condition of the ammonio-cupric oxide.

If dry cotton is treated with the ammonio-copper solution, it is first converted into a jelly and then dissolved. When the solution is acidified, the cotton is reprecipitated, and the weight of the dry precipitate is exactly the same as that of the original cotton. This dried precipitate gives a blue tint with iodine in presence of dilute sulphuric acid, and consists of a modified form of cellulose. It dissolves in a hot solution of zinc chloride, and separates out on cooling, thus differing both from cellulose and the other modifications of cellulose. It was dissolved in hydrochloric acid and the solution examined with the polarimeter. This solution was at first perfectly inactive, but after some time it acquired a dextrorotatory power, owing to decomposition of the cellulose by the acid.

It follows, that the rotatory power of solutions of cellulose in the ammonio-copper solution is not due to any rotatory power of the cellulose, which is optically inactive, but to the action of the cellulose in modifying the rotatory power of the optically active ammonio-copper solution.

C. H. B.

**Rotatory Power of Solutions of Cellulose in Schweizer's Solution.** By A. LEVALLOIS (*Compt. rend.*, 100, 456—458).—A reply to Béchamp (this vol., p. 369). The author maintains his former position.

C. H. B.

**Sugar from Agar-Agar. A New Acid from Arabinose. Classification of the Carbohydrates which form Jellies.** By R. W. BAUER (*J. pr. Chem.* [2], 30, 367—388).—Agar-agar, a gelatinous substance prepared from sea-weed, contains a carbohydrate closely resembling but not identical with the galactine described by Muntz

(Abstr., 1882, 707). When boiled with dilute acids, it is converted into lactose. The lactose from agar-agar and the lactose from milk-sugar, when treated with bromine and oxide of silver, yield lactonic acid, which is characterised by the sparing solubility of its cadmium salt,  $C_6H_5O_6Cd + 1\frac{1}{2}H_2O$ , in cold water. The molecular rotation of the lactose from agar-agar is  $[\alpha]_D = +79.9^\circ$ , and that of arabinose is  $[\alpha]_D = 99.6^\circ$ . Reichardt's statement (this Journal, 1875, 1179) that the carbohydrate contained in agar-agar is arabinose is therefore incorrect.

On treatment with bromine and oxide of silver, arabinose yields arabonic acid. The cadmium salt of this acid dissolves freely in cold water. Arabinose is obtained from gum tragacanth, cherry gum, and certain varieties of gum arabic. That kind of gum arabic which yields a considerable quantity of mucic acid on oxidation, forms lactose when boiled with dilute acids. The author proposes to classify the starches and other carbohydrates which are capable of gelatinising, according to the glucoses which they yield. W. C. W.

**Extraction of Amines from Commercial Methylamine.** By A. MULLER (*Bull. Soc. Chim.*, 42, 202—206).—In order to separate the amines in commercial methylamine the author uses the two following processes:—In the first, which is employed for the extraction of the lower amines, the methylamine is agitated with one and a half times its volume of potash solution ( $50^\circ$  Beaumé), and the gas which is evolved is condensed in dilute hydrochloric acid. After the mixture has been warmed to  $20$ — $22^\circ$ , and no further evolution of gas occurs, the operation is stopped, and the solution of the hydrochloride evaporated until it has a boiling point of about  $150^\circ$ . The solution is then cooled and the magma pressed from adhering liquid. The mother-liquor is concentrated until it has a boiling point of about  $180^\circ$ , and when cool is separated from the solid matter.

The precipitate obtained from the first liquid contains ammonium chloride and methylamine hydrochloride, whilst the mother-liquor which has been evaporated contains ethylamine, dimethylamine, and trimethylamine hydrochlorides. The precipitate is washed with cold absolute alcohol and then extracted with boiling absolute alcohol. The liquid, which should be filtered hot, deposits methylamine hydrochloride as it cools. The original mother-liquor is acted on with concentrated potash solution, and the gas, after passing through a tube containing fragments of caustic potash, is conducted into absolute alcohol. A portion of this solution, when cold, is titrated with sulphuric acid, and to the remainder ethyl oxalate is added to the extent of one-fifth of a molecular proportion for every molecular proportion of sulphuric acid that would be necessary to neutralise it. After standing for twelve hours the trimethylamine, which is unaffected, is separated from the liquid by distillation from a water-bath. The solution remaining in the retort is strongly concentrated by evaporation, cooled to  $0^\circ$ , and the precipitate separated. This consists chiefly of dimethyloxamide, and is recrystallised, the first fractions of the precipitate being rejected. It is then decomposed with potash, and the gas, after desiccation over solid potash, is received in absolute alcohol. The

ethylamine, when present in considerable quantity, may be precipitated by alcoholic sulphuric acid, by which means the pure sulphate is obtained. The liquid from which the oxamides have been separated is diluted with five times its volume of water, heated to 50°, and milk of lime added, until a distinct smell is noticeable. The filtered liquid is evaporated nearly to dryness on the water-bath and treated with 5—6 times its weight of boiling alcohol (70 per cent.); this is filtered hot and evaporated until a pellicle is formed, when it is again filtered and evaporated to dryness. The powdered residue is extracted with boiling absolute alcohol, when almost pure calcium dimethyloxamate remains.

In order to extract the higher amines, the crude methylamine is four-fifths neutralised with hydrochloric acid and distilled. The distillate is completely neutralised with hydrochloric acid, and the solution of the hydrochlorides concentrated until it has a boiling point of 150°. After cooling, the precipitate, consisting mainly of ammonium chloride, is removed, and the liquid warmed with concentrated potash solution. After desiccation with solid potash, the amines are condensed. The liquid, after remaining for a day in contact with solid potash, is fractionally distilled. The fraction obtained between 40° and 90° is exactly neutralised with alcoholic sulphuric acid, which almost entirely precipitates the sulphates of ethylamine and amylamine. These are removed, and the alcohol distilled from the liquid, when the soluble sulphates remain; these are decomposed by potash, and the amines condensed in water. The aqueous solution, a portion of which has been previously titrated, is then precipitated with ethyl oxalate. The oxamides are fractionally crystallised; when decomposed they yield propylamine and butylamine. Small quantities of triamines can also be obtained from this fraction. The fraction which passes over between 90—120° is principally amylamine. It is neutralised with alcoholic sulphuric acid, and the precipitate, after being repeatedly washed with absolute alcohol, is pressed and dried at 110°. The pure amylamine sulphate is dissolved in water and decomposed with potash solution (50° Beaumé), when the amylamine floats on the surface of the liquid. This is rectified by distillation at 95° from solid potash. The small fraction which is obtained between 120° and 190° contains one or more triamines, which are nearly insoluble in water.

W. R. D.

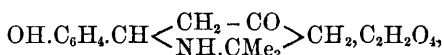
**Compounds of Diacetonamine with Aldehydes.** By O. ANTRICK (*Annalen*, **227**, 365—383).—After referring to the investigations of Heintz (*Annalen*, **193**, 62) and E. Fischer (*Abstr.*, 1884, 53 and 1290), the author describes the preparation of *valerodiacetonamine*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH} < \begin{smallmatrix} \text{CH}_2\text{-CO} \\ \text{NH}\cdot\text{CMe}_2 \end{smallmatrix} > \text{CH}_2$ , by boiling valeraldehyde with an alcoholic solution of diacetonamine oxalate for 10 hours in a flask with a reflux condenser. On recrystallisation from alcohol, the oxalate is obtained in needle-shaped crystals melting with decomposition at 190°. The base prepared by decomposing the oxalate with potash, crystallises in needles, which begin to soften at 15° and melt at 21°. It is soluble in ether, alcohol, benzene, and light petroleum. The

*hydrochloride* and *sulphate* are very soluble in water; the *platinochloride* crystallises in prisms, soluble in alcohol and in hot water. When strong hydrobromic acid is added to an alcoholic solution of valerodiacetonamine, the *hydrobromide* is deposited in the form of a crystalline precipitate, soluble in alcohol and in water. On reduction with sodium amalgam, valerodiacetonamine appears to yield valerodiacetonine.

*Ænanthodiacetonamine*,  $C_6H_{13}.CH<\frac{CH_2-CO}{NH.CMe_2}>CH_2$  (m. p.  $29.5^\circ$ ), is soluble in alcohol, ether, chloroform, benzene, and light petroleum. The salts of this base are freely soluble, with the exception of the neutral oxalate.

*Cinnamodiacetonamine*,  $CHPh : CH.CH<\frac{CH_2-CO}{NH.CMe_2}>CH_2$ , forms needle-shaped crystals containing  $\frac{1}{2}$  mol.  $H_2O$ , which melt at  $49^\circ$ . The base is freely soluble in ether, alcohol, chloroform, benzene, and light petroleum. The salts, excepting the oxalate, dissolve freely in water and alcohol. The *platinochloride* is deposited from the concentrated alcoholic solution in prisms.

*Parahydroxybenzaldiacetonamine oxalate*,



is sparingly soluble in alcohol and in cold water. It melts at  $193^\circ$  with decomposition.

*Anisodiacetonamine*,  $C_{14}H_{19}NO_2$ , is freely soluble in ether, alcohol, benzene, and light petroleum. The oxalate is sparingly soluble in water and alcohol.

*Orthonitrobenzaldiacetonamine*,  $C_{13}H_{16}N_2O_3$ , is an oily liquid miscible with alcohol and chloroform. The *oxalate* is sparingly soluble in water and alcohol. The *hydrochloride* crystallises in prisms. The *platinochloride* dissolves in hot water. Attempts to convert orthonitrobenzaldiacetonamine into the corresponding amido-compound were unsuccessful.

*Metanitrobenzaldiacetonamine* is a thick liquid miscible with ether, alcohol, benzene, chloroform, and carbon bisulphide. It forms crystalline salts. When reduced with stannous chloride, it is converted into the corresponding amido-compound, which is also a non-crystallisable liquid. The acid oxalate,  $C_{13}H_{16}N_2O.C_2H_2O_4$ , dissolves freely in water.

*Paranitrobenzaldiacetonamine* crystallises in needles melting at  $142.5^\circ$ . It is soluble in alcohol, ether, and chloroform. The *oxalate* is insoluble in alcohol. The *hydrochloride* forms needle-shaped crystals which contain 1 mol.  $H_2O$ . The *platinochloride* is deposited from an aqueous solution in flat prisms.

*Paramidobenzaldiacetonamine* is an alkaline liquid soluble in hot water and also in alcohol, ether, and chloroform. The acid *oxalate* is soluble in alcohol and water.

When diacetonamine is left in contact with solid potash, the anhydride,  $C_{12}H_{24}N_2O$ , separates out as a crystalline mass melting at  $83^\circ$ . It is soluble in alcohol, chloroform, and benzene. When boiled with water, it is decomposed into ammonia and mesityl oxide.

W. C. W.



**Hydroxyphosphinic Acids.** By W. FOSSEK (*Monatsh. Chem.*, **5**, 627—642).—The *hydroxyphosphinic acids* are the compounds formed by the action of phosphorus trichloride on aldehydes (Abstr., 1884, 833). Phosphorus trichloride (1 mol.) is carefully added to the aldehyde (4 mols.), and the unstable oil formed, is decomposed by the addition of 20 times its weight of water. In this manner, a liquid is obtained separating into two layers, the upper representing two-thirds of the aldehyde employed, and the lower containing a solution of the hydroxyphosphinic acids.

*Hydroxyamylphosphinic acid*,  $C_5H_{13}PO_4$ , crystallises from water in lustrous scales, resembling spermaceti; by slowly evaporating its alcoholic solution, it may be obtained in well-defined forms consisting of six-sided tablets of the monosymmetric system, melting at  $183-184^\circ$ . The *hydrogen barium salt*,  $(C_5H_{12}PO_4)_2Ba$ , crystallises from dilute alcohol or water in stellate groups; the normal salt,  $C_5H_{11}PO_4Ba + 2H_2O$ , forms a white crystalline powder, less soluble in cold than in hot water. The *calcium salts* resemble the barium compounds. The *silver salt*,  $C_5H_{11}PO_4Ag_2$ , and *lead salt*,  $C_5H_{11}PO_4Pb$ , are obtained as white precipitates, by adding silver nitrate and lead acetate to solutions of the acid neutralised by ammonia. Phosphorus pentachloride converts hydroxyamylphosphinic acid into an oil boiling at  $134-140^\circ$ , under a pressure of 22 mm. This compound has the formula  $C_5H_{10}POCl_3$ , showing the presence of three hydroxyl-groups in the hydroxyphosphinic acid; when decomposed with water it yields an acid, apparently amylchlorophosphinic acid,  $C_5H_{12}ClPO_3$ .

Hydroxyamylphosphinic acid is but incompletely decomposed by nitric acid or aqua regia, and is not attacked when boiled with aqueous alkalis; potassium permanganate resolves it into isovaleraldehyde and phosphoric acid. By heat, hydroxyamylphosphinic acid is resolved into isovaleraldehyde and phosphorous acid, the latter yielding phosphine and phosphoric acid as further products of decomposition.

The author considers that this compound has the constitution  $C_4H_9.CH(OH).PO(OH)_2$ .

*Hydroxyisobutylphosphinic acid*,  $C_4H_7.CH(OH).PO(OH)_2$ , resembles the amyl compound in physical and chemical characters; it crystallises in lustrous rhombic tables melting at  $168-169^\circ$ .

P. P. B.

**Formation of Oxymethylene from Ethyl Nitrate.** By L. PRATESI (*Gazzetta*, **14**, 221—226).—When platinum foil heated to low redness is partly immersed in ethyl nitrate, a powerful reaction takes place, and the heat developed gradually vaporises the liquid which is then decomposed. By arranging a suitable apparatus in which a stream of ethyl nitrate is allowed to flow slowly into a test-tube containing a piece of platinum heated to low redness, the reaction can be easily regulated, care being taken that part of the platinum projects above the surface of the liquid. Large quantities of carbonic anhydride and nitric oxide are evolved, and a liquid distils over, accompanied by a yellowish-white amorphous substance. The latter contains nitrogen,

but has not been further examined at present. The liquid was found to contain oxymethylene in small quantity. C. E. G.

**Isomeric Ketones.** By G. CHANCEL (*Compt. rend.*, **99**, 1053—1056).—Amongst the ketones with an odd number of carbon-atoms, there are always two isomerides, one a simple, the other a mixed ketone, which yield the same two acids on oxidation. For example, dipropyl ketone and ethyl-butyl ketone both yield propionic and butyric acids; diethyl ketone and methyl propyl ketone both yield acetic and propionic acids. The author has previously shown (*Abstr.*, 1882, 710; 1883, 914) that alkyl-nitrous acids are easily obtained by the action of nitric acid on ketones, and that in the case of mixed ketones the nitrous groups always attach themselves to the higher alkyl radicle. This reaction may be employed for the purpose of distinguishing between isomerides of the kind referred to above. Diethyl ketone, for example, yields ethyl-nitrous acid, whilst methyl propyl ketone yields propyl-nitrous acid. The alkyl-nitrous acids may be converted into the corresponding potassium and silver salts, the properties of which are very characteristic. C. H. B.

**Acetonylacetone.** By C. PAAL (*Ber.*, **18**, 58—60).—The author has already described the formation of *acetonylacetone*,  $C_6H_{10}O_2$ , when pyrotritartaric acid is heated with water at  $150$ — $160^\circ$  (this vol., p. 249). It is a colourless, mobile liquid of pleasant odour, and boils at  $187$ — $188^\circ$  (uncorr.). It is miscible in all proportions in water, ether, and alcohol. It is resinified by sulphuric acid even in the cold. Contrary to Weltner's experience (*Abstr.*, 1884, 746), the author also obtained this double ketone by heating ethyl acetonyl-acetoacetate with water at  $160^\circ$ . *Diisonitrosoacetonylacetone* is formed by the action of hydroxylamine on acetonylacetone. It crystallises in prisms easily soluble in mineral acids, alkalis, and boiling water, and melts at  $134$ — $135^\circ$ . *Diphenylhydrazineacetonylacetone* forms glistening plates, melting at  $120^\circ$  and easily soluble in alcohol, ether, and benzene. L. T. T.

**Method of Preparing Diacetyl Cyanide.** By S. KLEEMANN (*Ber.*, **18**, 256—257).—A convenient and cheap method of preparing diacetyl cyanide is the following: 32 grams of potassium cyanide are placed in a flask provided with a reflux condenser, six or eight times the weight of benzene is added, and then 50 grams of acetic anhydride; the whole being boiled for five hours with frequent agitation. The product is filtered, the residue washed with benzene, and the filtrate freed from the latter by distillation, when a brown oil is obtained which crystallises in the cold. The crystals are purified by distillation in a current of steam. Diacetyl cyanide melts at  $69^\circ$ , boils at  $210^\circ$  (corr.), and has a vapour-density of 4.44 to 4.70 (theory requires 4.77). It dissolves readily in alcohol, ether, and benzene, and is moderately soluble in hot water. Hydrochloric acid converts it into hydrocyanic and acetic acids. A. K. M.

**Action of Heat and Water on the Halogen-substituted Acids of the  $C_nH_{2n}O_2$  Series. II.** By H. BÉCKURTS and R. OTTO (*Ber.*, 18, 222—238). For first paper see *Abstr.*, 1881, 574.

*$\alpha$ -Bromopropionic Acid.*—The silver salt of this acid cannot be obtained free from silver bromide, either by precipitation from an alkali salt, or by neutralising the acid with silver carbonate, so that the action of heat on the dry salt could not be tried. When the acid (30 grams) is diluted with water, neutralised with silver oxide (28 grams), and heated on the water-bath, the whole of the silver is soon precipitated as bromide, whilst the filtrate from this contains *ethylidenelactic acid*,  $CHMeBr.COOAg + H_2O = AgBr + OH.CHMe.COOH$ . When an aqueous solution of  $\alpha$ -bromopropionic acid is neutralised with potassium carbonate and the solution placed in a desiccator to crystallise at the ordinary temperature, crystals of potassium bromide appear, and the solution gradually becomes acid from the formation of lactic acid; if this be neutralised with a further quantity of carbonate, the reaction goes on until finally the whole of the  $\alpha$ -bromopropionic acid is converted into ethylidenelactic acid. When a solution of barium  $\alpha$ -bromopropionate is left to evaporate in a desiccator, an amorphous mass is obtained which is completely soluble in cold absolute alcohol; on evaporating this solution, a brittle partly translucent and partly transparent vitreous residue is left.

*$\beta$ -Iodopropionic Acid.*—The silver salt of this acid could not be obtained free from iodide, as it parts with its halogen even more readily than  $\alpha$ -bromopropionic acid. When an aqueous solution of the acid (40 grams) is warmed for a short time with silver carbonate, the precipitate consists entirely of silver iodide, whilst the solution contains *hydracrylic acid*. This reaction may also be effected at the ordinary temperature.

*$\beta$ -Chloropropionic Acid.*—The silver salt cannot be obtained free from silver chloride, and the potassium and sodium salts also decompose at the ordinary temperature with separation of metallic chlorides.

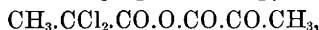
*$\beta$ -Bromopropionic Acid*, obtained by heating hydracrylic acid with aqueous hydrobromic acid, forms small lustrous scales melting at 61—62°, and readily soluble in water. Neither the silver, potassium, nor sodium salt could be obtained free from bromide.

*$\alpha$ -Dichloropropionic Acid.*—The authors previously stated (*Abstr.*, 1877, 181; 1878, 291) that this acid is decomposed by silver oxide or carbonate, with production of either pyruvic or monochloracrylic acid, according to the conditions of the experiment. On repeating the experiment, it was found, however, that the supposed chloracrylic acid is a mixture of pyruvic and dichloropropionic acids, the percentage of chlorine in the mixture being about the same as that required for chloracrylic acid. The action of heat on silver  $\alpha$ -dichloropropionate in the presence of water may therefore be expressed thus:—



and is analogous to the decomposition of silver dichloracetate. If in the above reaction equal molecular proportions of  $\alpha$ -dichloropropionic acid and of silver oxide are taken, pyruvic acid alone is obtained. Dry silver  $\alpha$ -dichloropropionate decomposes with explosive violence

when heated at  $60^{\circ}$ , the chief products being silver chloride and the mixed anhydride of  $\alpha$ -dichloropropionic and pyruvic acids,



besides small quantities of carbonic anhydride and carbonic oxide; the mixed anhydride is a viscous yellow liquid having an odour like that of phosphoric chloride, and boiling between  $160^{\circ}$  and  $170^{\circ}$ ; it takes up water with great readiness and yields a mixture of the two acids.

*$\alpha$ -Dibromopropionic Acid.*—The silver salt of this acid is more unstable than that of the corresponding chlorinated acid, and could not be obtained in the dry state. When the acid is heated with silver carbonate and water, it suffers decomposition perfectly analogous to that of  $\alpha$ -dichloropropionic acid.

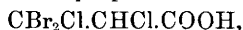
*$\alpha$ - $\beta$ -Dibromopropionic Acid.*—The silver salt does not exist in the dry state. When the acid (1 mol.) is heated in aqueous solution with silver carbonate ( $\frac{1}{2}$  mol.), silver bromide and bromolactic acid,  $\text{OH.CH}_2.\text{CHBr.COOH}$ , are formed. If, however, equal molecular proportions of  $\alpha$ - $\beta$ -dibromopropionic acid and silver oxide be heated together in the presence of water, the whole of the bromine is separated as silver bromide, whilst *glyceric acid*,  $\text{OH.CH}_2.\text{CH(OH).COOH}$ , is produced.

A. K. M.

**$\beta$ -Dibromo-dichloropropionic and  $\beta$ -Bromodichloracrylic Acids.** By C. F. MABERY and H. H. NICHOLSON (*Amer. Chem. J.*, 6, 165—170).— *$\beta$ -Dibromodichloropropionic acid*,  $\text{C}_3\text{H}_2\text{Cl}_2\text{Br}_2\text{O}_2$ , is formed by the direct union of chlorine with  $\beta$ -dibromacrylic acid, which takes place most satisfactorily at  $100^{\circ}$ . It is best purified by crystallisation from carbon bisulphide, and forms oblique prisms melting at  $100^{\circ}$ , and subliming slowly at higher temperatures. It is sparingly soluble in water, more soluble in hot than in cold chloroform, and easily soluble in ether and alcohol. The salts of this acid are unstable; the *calcium* salt,  $\text{Ca}(\text{C}_3\text{HCl}_2\text{Br}_2\text{O}_2)_2 + 1\frac{1}{2}\text{H}_2\text{O}$ , crystallises in clumps of needles; the *potassium* salt,  $\text{KC}_3\text{HCl}_2\text{Br}_2\text{O}_2 + 2\text{H}_2\text{O}$ , loses its water of crystallisation when dried over sulphuric acid.

*$\beta$ -Bromodichloracrylic acid*,  $\text{C}_3\text{HCl}_2\text{BrO}_2$ , is obtained by decomposing the above acid with an alkaline hydroxide in the cold, preferably barium hydroxide. It is very soluble in hot, sparingly in cold water, and easily soluble in carbon bisulphide, chloroform, ether, and alcohol. It forms pearly scales melting at  $75$ — $78^{\circ}$ . Water at  $20^{\circ}$  dissolves 4.74—4.79 per cent. of the acid.

The *barium* salt,  $\text{Ba}(\text{C}_3\text{Cl}_2\text{BrO}_2)_2 + 3\text{H}_2\text{O}$ , forms prismatic crystals, less soluble in cold than hot water; the *calcium* salt,  $\text{Ca}(\text{C}_3\text{Cl}_2\text{BrO}_2)_2 + 3\text{H}_2\text{O}$ , crystallises in rhombic plates; the *potassium* salt,  $\text{KC}_3\text{Cl}_2\text{BrO}_2$ , forms minute, easily soluble, prismatic crystals; the *silver* salt,  $\text{AgC}_3\text{Cl}_2\text{BrO}_2$ , is obtained as a curdy precipitate and crystallises from hot water in irregular rhombic plates. Since according to Hill,  $\beta$ -dibromacrylic acid has the constitution  $\text{CBr}_2:\text{CH.COOH}$  (*Abstr.*, 1883, 310),  $\beta$ -dichloro-dibromopropionic acid must be



and  $\beta$ -bromodichloracrylic acid,  $\text{CBrCl}:\text{CCl.COOH}$ .

P. P. B.

**$\beta$ -Bromotetrachloropropionic Acid.** By C. F. MABERY (*Amer. Chem. J.*, **6**, 155—157).—Chlorine reacts with a solution of bromopropionic acid in chloroform, forming  $\beta$ -bromotetrachloropropionic acid,  $\text{CBrCl}_2\text{.CCl}_2\text{.COOH}$ ; this is sparingly soluble in cold carbon bisulphide and chloroform, but more easily when heated; it melts and decomposes at  $225^\circ$ . Its salts are extremely unstable.

The statement previously made (Mabery and Robinson, *Abstr.*, 1884, 664) to the effect that chlorine combines with bromopropionic acid to form bromodichloracrylic acid is incorrect. P. P. B.

**Palmitic Acid and the Palmitins.** By R. H. CHITTENDEN and H. E. SMITH (*Amer. Chem. J.*, 1884, 217—233).—The wax of *Myrica cerifera* was taken as a very suitable raw material, since lauric acid is the only other acid contained. It was saponified and the palmitic acid obtained, purified by repeated recrystallisation from hot alcohol. 100 parts of absolute alcohol at  $19.5^\circ$  dissolve 9.209—9.428 parts of the acid. All methods for precipitating palmitic acid yield low results, more than 96 per cent. never being obtained.

A number of determinations of the solubility of the calcium, barium, magnesium, and lead salts in absolute alcohol are given; their solubility is greatly increased by the addition of a very small quantity of acetic acid. Instead of separating it as a salt, the authors determine the palmitic acid in the glyceryl palmitates by saponification, precipitation with hydrochloric acid, and drying. The different palmitins are best separated by crystallisation from alcohol. Tripalmitin is almost entirely insoluble in cold alcohol (0.0053—0.0043 in 100 parts), dipalmitin is somewhat more soluble (0.2097 at  $20^\circ$  to 0.5040 at  $27^\circ$  in 100 parts), and monopalmitin easily so (4.135 at  $21^\circ$  to 5.306 at  $22.5^\circ$  in 100 parts). According to Berthelot, the different palmitins may be obtained by heating palmitic acid and glycerol to different temperatures; but the authors find that a mixture of palmitins is always thus formed. Better yields are obtained by using the ingredients in the calculated proportions, and, in the case of the mono- and di-palmitins, heating at a low temperature for a long time.

Monopalmitin melts at  $63^\circ$  and solidifies at  $62.25$ — $62.75^\circ$  (Berthelot,  $58^\circ$ ). Dipalmitin melts at  $61^\circ$  and solidifies at  $57^\circ$  (Berthelot,  $59^\circ$  and  $51^\circ$ ). Tripalmitin melts at  $62$ — $64^\circ$  and solidifies at  $45.5$ — $47^\circ$  (Berthelot,  $61^\circ$  and  $46^\circ$ ); a variation of melting point was here noticed similar to that mentioned by Duffy and by Maskelyne. There also appears to exist a compound of 3 parts dipalmitin with 1 part tripalmitin; its solubility is intermediate between that of dipalmitin and tripalmitin; it melts at  $68$ — $69^\circ$ , and is quite solid at  $65$ — $64^\circ$ .

H. B.

**Arachidic Acid and Nondecyllic Acid.** By A. SCHWEIZER (*Arch. Pharm.* [3], **22**, 753—775).—The author shows that arachidic acid is a normal acid by synthesising it from stearic acid by the following process:—Octodecyl alcohol prepared from stearic acid by Krafft's method (*Abstr.*, 1883, 1076) is converted into the iodide; this is then treated with ethylic acetosodacetate, when ethylic stearyl-acetoacetate is formed, from which, by saponification with alcoholic potash, an acid is obtained showing complete identity with the natural

arachidic acid. This synthesis confirms Krafft's view that the naturally occurring fatty acids are all normal acids. Arachidic acid melts at  $75.5^{\circ}$ . The *methyl salt*,  $C_{19}H_{39}.COOMe$ , melts at  $53^{\circ}$  and distils at  $285-286^{\circ}$  under 100 mm. pressure. The *ethyl salt*,  $C_{19}H_{39}.COOEt$ , melts at  $49.5^{\circ}$  and boils at  $295-297^{\circ}$  under 100 mm. pressure.

*Normal nondecyllic acid*,  $C_{18}H_{37}.COOH$ , is prepared by heating octodecyl iodide with mercuric cyanide in sealed tubes for some hours at  $120^{\circ}$  and decomposing the octodecyl cyanide formed, by boiling it with alcoholic potash. It crystallises in small silvery plates, melts at  $66.5^{\circ}$  and distils, without decomposition, at  $297-298^{\circ}$  (uncorr.) under 100 mm. pressure. The following salts were prepared and analysed:  $-C_{19}H_{37}O_2Ag$ ;  $(C_{19}H_{37}O_2)_2Ca$ ;  $(C_{19}H_{37}O_2)_2Ba$ ; and  $(C_{19}H_{37}O_2)_2Cu$ .

*Octodecyl iodide*, prepared by the action of phosphorus and iodine on the alcohol, crystallises in small, lustrous white plates, melts at  $42-43^{\circ}$ , and decomposes on further heating. It is readily soluble in light petroleum, benzene, and chloroform.

Stearyl chloride is obtained as a yellow oil by the action of phosphoric chloride on stearic acid. When treated with mercuric cyanide and the product of the reaction boiled with potash, an acid is obtained which, from its reaction with hydroxylamine, would appear to be a carboketonic acid ( $C_{17}H_{35}.CO.COOH$  ?); the quantity obtained, however, was too small for complete investigation.

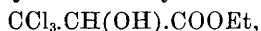
A. J. G.

**Constituents of Wool-grease.** By A. BUISINE (*Bull. Soc. Chim.*, **42**, 201-202).—Hartmann and Schulze have shown that the wool-grease of sheep contains the salts of cholesterol and ischolesterol. From the analysis of many specimens, the author finds that it also contains ceryl cerotate and other homologous ethereal salts, which may be isolated in the following manner:—The fat is saponified with alcoholic potash at  $100^{\circ}$  in a closed flask, and, after distillation of the alcohol, the soap is freed from excess of alkali by repeated washing with salt solution. The potassium soap is converted into a barium soap, which is dried and boiled, first with alcohol and ether, and then with alcohol which extracts chlorestrol with ceryl alcohol, and other homologous alcohols. The ceryl alcohol, which is the least soluble in alcohol, is purified by recrystallisation.

The barium soap when decomposed furnishes cerotic acid and other homologous acids. The ceryl alcohol and cerotic acid were both obtained pure, and fully identified by their chemical and physical properties, as well as by an examination of certain of their derivatives.

W. R. D.

**Monohalogen-derivatives of Acrylic Acid.** By R. OTTO and H. BECKURTS (*Ber.*, **18**, 239-246).—The acid obtained by Pinner and Bischoff (this Journal, 1876, i, 554) by the action of zinc and hydrochloric acid on ethyl trichlorethylidenelactate,



and also by Wallach and Hunäus (*Annalen*, **193**, 28) from chloralide, is undoubtedly  $\beta$ -chloroacrylic acid,  $CHCl:CH.COOH$ . Baudrowsky (Abstr., 1883, 314) obtained it more recently by the action of hydro-

chloric acid on propargylic acid. A second monochloracrylic acid obtained by Werigo and Werner (this Journal, 1874, 242) by the action of barium hydroxide on ethyl  $\alpha$ - $\beta$ -dichloropropionate, differed widely in its properties from the  $\beta$ -acid, and would therefore have been generally accepted as the  $\alpha$ -modification, had not the authors of this paper described a third modification (see this vol., p. 506, also Abstr., 1878, 291) obtained by the action of silver oxide on  $\alpha$ -dichloropropionic acid, and which they have now shown to be a mixture of  $\alpha$ -dichloropropionic and pyruvic acids. With the view of obtaining  $\alpha$ -chloracrylic acid, the authors have treated  $\alpha$ -dichloropropionic acid with potash in different proportions and in different degrees of concentration; they recommend that 20 grams of the acid should be heated for 4—5 hours with a solution of 24 grams potash in 200 c.c. absolute alcohol. The  $\alpha$ -chloracrylic acid obtained melts at 65°, crystallises in concentrically-grouped white needles of characteristic acrid odour, and volatilises readily at the ordinary temperature. It is evidently identical with the acid prepared by Werigo from  $\alpha$ - $\beta$ -dichloropropionic acid (*loc. cit.*). The potassium salt,  $C_3H_2ClKO_2 + H_2O$ , barium salt,  $(C_3H_2ClO_2)_2Ba + 2H_2O$ , and silver salt,  $C_3H_2ClAgO_2$ , are described. When  $\alpha$ -chloracrylic acid is heated with 40 per cent. hydrochloric acid at 100°, it is converted into  $\alpha$ - $\beta$ -dichloropropionic acid.

$\alpha$ -Bromacrylic acid was obtained by Tollens and Philippi (this Journal, 1874, 680) by the action of alcoholic potash on  $\alpha$ -dibromopropionic acid. It agreed in its properties with the acid obtained by Tollens and Wagner from  $\alpha$ - $\beta$ -dibromopropionic acid, except that the potassium salts of the two acids were said to crystallise differently. Both bromacrylic acids, however, are converted into  $\alpha$ - $\beta$ -dibromopropionic acid by the addition of hydrobromic acid. Wallach and Riencke (Abstr., 1878, 403) prepared another bromacrylic acid from ethyl tribromolactate by reduction with zinc and hydrochloric acid, and also from bromalide; this can only be the  $\beta$ -compound. It may therefore be concluded that both the dibromopropionic acids yield  $\alpha$ -bromacrylic acid just as the two dichloropropionic acids yield  $\alpha$ -chloracrylic acid, and this is also proved by the crystallographic researches of Haushofer (Abstr., 1882, 190). According to Baudrowsky, propargylic acid is converted by hydrobromic acid into a bromacrylic acid differing from Wallach's  $\beta$ -acid, but that it is the  $\alpha$ -compound does not seem probable from the action of hydrochloric acid on propargylic acid (see above). If the chloracrylic acid so obtained be identical with Wallach's acid melting at 84—85°, the iodacrylic acid, melting at 140°, formed from hydriodic and propargylic acids, must likewise be a  $\beta$ -compound.

A. K. M.

$\alpha$ - and  $\beta$ -Chlorodibromacrylic Acids. By C. F. MABERY and R. LLOYD (*Amer. Chem. J.*, **6**, 157—165).— $\alpha$ -Chlorodibromacrylic acid,  $C_3HClBr_2O_2$ , is obtained by adding bromopropionic acid to a solution of bromine monochloride in chloroform prepared by saturating bromine with chlorine at 0°, and after dissolving the product in chloroform again saturating it with chlorine at 0°. The acid is sparingly soluble in cold, very soluble in hot water, more soluble in hot than in cold carbon bisulphide, and very soluble in chloroform. It melts at 104°. From its solutions in carbon bisulphide, it crystallises

in triclinic prisms; a description of the crystals is given. Water at 20° dissolves from 5.18 to 5.68 per cent. of the acid. *Barium α-chlorodibromomacrylate*,  $\text{Ba}(\text{C}_3\text{ClBr}_2\text{O}_2)_2 + 3\text{H}_2\text{O}$ , crystallises in long flat prisms; it is more soluble in cold than in hot water. Water at 20° dissolves 20.46—20.47 per cent. of this salt. The *calcium salt*,  $\text{Ca}(\text{C}_3\text{ClBr}_2\text{O}_2)_2 + 2\frac{1}{2}\text{H}_2\text{O}$ , crystallises in irregularly branching needles; the *potassium salt* forms deliquescent amorphous crusts, and the *silver salt*,  $\text{AgC}_3\text{ClBr}_2\text{O}_2$ , is obtained as a curdy precipitate by adding silver nitrate to a solution of the barium salt; crystallised from hot water, it forms rhombic prisms.

*β-Chlorodibromomacrylic acid*,  $\text{C}_3\text{HClBr}_2\text{O}_2$ , is formed by decomposing chlorotribromopropionic acid with baryta-water in the cold (comp. Abstr., 1884, 663). The acid is purified by crystallisation from water; it is easily soluble in ether and alcohol, less soluble in carbon bisulphide and chloroform. From its solutions in carbon bisulphide, it crystallises in oblique prisms melting at 99°. Water at 20° dissolves 2.69—2.50 per cent. of this acid. *Barium β-chlorodibromomacrylate*,  $\text{Ba}(\text{C}_3\text{ClBr}_2\text{O}_2)_2 + 3\text{H}_2\text{O}$ , crystallises from water in oblique slender prisms, is somewhat more soluble in cold water than the corresponding salt of the α-acid; water at 20° dissolves 25.9—26.04 per cent. of the salt. The *calcium salt* crystallises in stellate groups of needles; it is less soluble in water than the salt of the α-acid. A silver salt could not be prepared, inasmuch as the acid is decomposed and silver bromide formed. The formation of the β-acid from chlorotribromopropionic acid, shows it to have the constitution  $\text{CBrCl} : \text{CBr}.\text{COOH}$ , and therefore the formula  $\text{CBr}_2 : \text{CCl}.\text{COOH}$  must be assigned to the α-acid.

P. P. B.

**Diallyloxalic Acid.** By E. SHATZKY (*J. Russ. Chem. Soc.*, 1885, 61).—The molecular refraction of the acid  $\text{C}_{18}\text{H}_{12}\text{O}_3$  was determined at 18.6°, benzene being used as a solvent, and the following numbers were found:—

$\frac{n_a - 1}{d}$	P. $\frac{n_a - 1}{d}$	$R_a$	Diff.	$\frac{A - 1}{d}$	P. $\frac{A - 1}{d}$	$R_A$	Diff.
0.4487	69.99	64.6	5.39	0.42991	67.07	63.07	4.00

The difference of about 4 units between the values calculated and those found is in accordance with Brühl's law, the compound containing two allyl-groups, and consequently two double linkings.

The salts of diallyloxalic acid ( $\text{NH}_4$ , Na, K, Li, Ag, Ca, Ba, Mg, Pb, Cu, Cd) were prepared, generally by saturating the acid with the carbonates of the metals, the zinc salts also, by precipitating the ammonium salt with zinc sulphate; in no instance were basic salts obtained. The calcium, barium, lead, and cadmium salts are more soluble in alcohol than in water; the salts obtained from alcoholic and aqueous solutions were identical, with the sole exception of the copper salt; this separated from aqueous solutions in an anhydrous



state, whilst the alcoholic solution yielded an amorphous mass, losing water at  $110^{\circ}$ . The silver salt could not be examined on account of its speedy decomposition. All the salts examined act on polarised light.

In order to establish the degree of saturation of the acid, the additive products of bromine and of hydrochloric acid with ethylic diallyloxalate were prepared; it took up 2 mols. Br and 2 mols. HCl. On treating the acid itself with bromine, an unstable tetrabromide was formed, giving off hydrogen bromide even at ordinary temperatures, and passing into a lactone,  $C_8H_{11}Br_3O_3$ , a crystalline substance, sparingly soluble in cold water, easily in alcohol, ether, and benzene. This melts at  $42-43^{\circ}$ , and solidifies again at  $30^{\circ}$ ; it is an analogue of the lactone obtained by Hjelt (Abstr., 1883, 456) from the additive product of bromine and diallylacetic acid. The lactone is but little decomposed by sodium carbonate, and the examination of the products obtained by the action of potassium hydroxide on it gave no satisfactory results.

Fuming hydriodic acid acts on diallyloxalic acid with formation of the acid  $C(C_2H_5)_2I.CO.OH$ ; this when treated with sodium amalgam yielded a product, the main portion of which, distilling at  $220-230^{\circ}$ , was identified as diallylacetic acid: the constitution of diallyloxalic acid must consequently be  $(CH_2:CH.CH_2)_2C(OH).CO.OH$ .

The oxidation of diallyloxalic acid with permanganate, nitric acid, silver oxide, and chromic acid, gives no definite results. Ethylic methoxydiallylacetate, a colourless liquid boiling at  $217-219^{\circ}$ , was prepared by treating ethylic diallyloxalate, first with sodium and then with methyl iodide. On saponifying the ethyl salt, a syrupy acid was obtained which did not crystallise. It was oxidised with nitric acid, and yielded an acid, forming soluble salts with silver, barium, zinc, and calcium, and an insoluble one with lead. The calcium, barium, and potassium salts were analysed, and the acid proved to be methoxycarballylic acid. The investigation is being continued with the view of obtaining citric acid from the oxidation products of methoxydiallylacetic acid.

A. T.

**Chlorocarbonylsulphamyl.** By H. SCHÖNE (*J. pr. Chem.* [2], 30, 416).—Chlorocarbonylsulphanryl,  $COCl.SC_6H_{11}$ , prepared by the action of carbonyl chloride on amyl thiohydrate, is a highly refractive liquid, boiling at  $190-195^{\circ}$ . On treatment with ammonia, it yields amidocarbonylsulphamyl,  $NH_2.CO.SC_6H_{11}$ , which crystallises in glistening scales melting at  $107^{\circ}$ ; with aniline it yields the anilide, which forms needle-shaped crystals melting at  $67^{\circ}$ . With carbamide, it forms a crystalline compound,  $CON_2H_3.COSC_6H_{11}$ , which melts at  $176^{\circ}$ .

W. C. W.

**Preparation of Ethylic Oxalate.** By E. SHATZKY (*J. Russ. Chem. Soc.*, 1885, 88).—The best method for preparing the ethereal salt, yielding 56.03 per cent. of the quantity required by theory, was found to be a modification of Löwig's process, consisting in a more prolonged action of the alcohol on oxalic acid, using a reflux condenser.

A. T.

**Method for Introducing Nitrogenous Radicles into Ethyl Malonate and Acetoacetate.** By F. JUST (*Ber.*, 18, 319—320).—By the action of benzanilidimidochloride (1 mol.) on ethyl monosodomalonate (1 mol.) in ethereal solution, a substance of the formula  $\text{PhN}:\text{CPh}.\text{CH}(\text{COOEt})_2$  is obtained. It forms large, hard, highly refractive crystals. The reaction has been further applied to the introduction of the group a second time into ethyl malonate and into ethylic acetoacetate, and the substituted acetocetates. The substances formed will be described later.

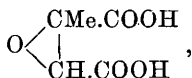
A. J. G.

**Hydroxymaleic and Hydroxycitraconic Acids.** By E. SCHERKS (*Annalen*, 227, 233—241).—There are three apparent exceptions to Erlenmeyer's law that compounds containing a hydroxyl-group attached to a double-linked carbon-atom are incapable of existence, namely, hydroxymaleic and dihydroxymaleic acids, described by Bourgoin (this Journal, 1873, 1021, and 1875, 356), and hydroxycitraconic acid prepared by Morawski (*ibid.*, 1875, 1252). The author has previously pointed out that the existence of hydroxymaleic acid is very doubtful. He now shows that there are not sufficient grounds for asserting the existence of dihydroxymaleic acid.

Morawski's hydroxycitraconic acid,  $\text{C}_5\text{H}_6\text{O}_5 + \text{H}_2\text{O}$ , forms transparent monoclinic crystals which effloresce on exposure to the air. The acid is soluble in water, alcohol, and ether. On evaporating the aqueous solution, a slight decomposition ensues; propaldehyde and carbonic anhydride are formed; 70 per cent. of the acid undergoes this decomposition when it is boiled with water in a flask fitted with a reflux condenser. The remainder unites with water, forming a hygroscopic acid of the composition  $\text{C}_5\text{H}_8\text{O}_6$ , probably the citratartaric acid of Carius. Although hydroxycitraconic acid does not combine with nascent hydrogen, it readily unites with hydrobromic acid to form a crystalline compound melting with decomposition at  $156^\circ$ . It has the composition  $\text{C}_5\text{H}_7\text{BrO}_5$ .

Of the three possible formulæ for the acid  $\text{C}_5\text{H}_6\text{O}_5$ ,

$\text{COOH}.\text{CMe}:\text{C}(\text{OH}).\text{COOH}$ ,  $\text{COOH}.\text{CHMe}.\text{CO}.\text{COOH}$ , or,



the author gives the preference to the latter. The second formula explains the formation of propaldehyde, but it neither explains the indifference of the acid to nascent hydrogen, nor its affinity for hydrobromic acid.

W. C. W.

**Derivatives of Pyruvic Acid.** By E. BAUMANN (*Ber.*, 18, 258—267).—The mercapturic acids were shown by Baumann and Preusse (*Abstr.*, 1882, 756) to be derivatives of pyruvic acid; the substituted  $\alpha$ -amido- $\alpha$ -thiolactic acid,  $\text{C}_9\text{H}_{10}\text{BrSNO}_2$ , obtained by the action of sulphuric acid on bromophenylmercapturic acid was then thought to be a substituted cystine. Kütz (*Zeit. f. Biol.*, 20, 1) has, however, shown that cystine has the formula  $\text{C}_6\text{H}_{12}\text{N}_2\text{S}_2\text{O}_4$ , and not  $\text{C}_3\text{H}_7\text{NSO}_3$ . The author likewise proved the formation of amidothioliactic acid

(cysteine) by the reduction of cystine (Abstr., 1884, 1382), this being represented by him as the bisulphide of amidothiolic acid,  $\text{COOH.C}_2\text{H}_5(\text{NH}_2).\text{S.S.C}_2\text{H}_5(\text{NH}_2).\text{COOH}$ , so that what were previously called substituted cystines should be termed substituted cysteines. The pyruvic acid formed by the action of alkali on mercapturic acid and on cysteine, which could not previously be isolated, may be readily separated by means of the phenylhydrazine reaction.

The formation of acetic acid and cysteine by the action of strong acids on mercapturic acids indicates that these are acetyl-derivatives of the cysteines. The following experiments are given in proof of the formula  $\text{PhS.CMe(NHAc).COOH}$ :—1. The mercapturic acids do not unite with potassium cyanate, whilst the cysteines obtained from them combine to form well-characterised uramido-acids,



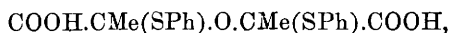
2. When bromophenylcysteine is warmed with acetic anhydride, the compound  $\text{C}_6\text{H}_4\text{BrS.CMe} \begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix}$  is formed by the abstraction of 1 mol.  $\text{H}_2\text{O}$ , whilst if the acetic anhydride is dissolved in 10 parts benzene, the corresponding mercapturic acid,  $\text{C}_6\text{H}_4\text{BrS.CMe(NHAc).COOH}$  ( $\alpha$ -acetamido- $\alpha$ -bromophenylthiolactic acid), is produced.

When the mercapturic acids are treated with potassium permanganate in slightly alkaline solution, they take up two atoms of oxygen, the product being a monobasic acid containing a sulphone-group. The oxidation products from chloro- and bromo-phenylmercapturic acids are respectively  $\text{C}_6\text{H}_4\text{Cl.SO}_2\text{CMe(NHAc).COOH}$  ( $\alpha$ -acetamido- $\alpha$ -chlorophenylsulphonepropionic acid) and  $\text{C}_{11}\text{H}_{12}\text{BrSNO}_5$ . These oxidation acids resemble the mercapturic acids in many respects: they are decomposed by strong acids with formation of acetic and monobasic amido-acids, whilst with alkalis they yield sulphinic acids (distinction from mercapturic acids) and pyruvic acid.

When equivalent quantities of thiophenol and pyruvic acid are dissolved in 30 parts of benzene and the whole gently heated, an additive compound,  $\text{C}_9\text{H}_{10}\text{SO}_3$ , is obtained, crystallising in short thick prisms melting at  $87^\circ$ . It is gradually decomposed by cold, instantly by hot water, and also when heated alone, the products being pyruvic acid and thiophenol. It is an acid, but no salts have been obtained owing to its ready decomposibility. Parabromothiophenol also combines with pyruvic acid, yielding the corresponding additive compound  $\text{C}_9\text{H}_9\text{BrSO}_3$ , which melts at  $114.5^\circ$ , and is likewise decomposed by water, acids, and alkalis into the mercaptan and pyruvic acid. These additive products are shown by their formation, decomposition, and chemical changes to be phenyl-derivatives of  $\alpha$ -thio- $\alpha$ -hydroxypropionic acid,  $\text{PhS.CMe(OH).COOH}$ . When thiophenylhydroxypropionic acid is gently heated in a current of dry hydrogen chloride, a hard crystalline mass is obtained, from which water extracts hydrochloric and pyruvic acids. The insoluble product is  $\alpha$ -dithiophenylpropionic acid,  $\text{CMe(SPh)}_2\text{COOH}$ ; it is readily soluble in alcohol, ether, benzene, and in alkalis and alkaline carbonates; it melts at  $113$ — $114^\circ$ . The barium salt,  $(\text{C}_{15}\text{H}_{13}\text{S}_2\text{O}_2)_2\text{Ba} + 2\text{H}_2\text{O}$ , forms long

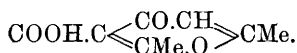
silky needles. Dithiophenylpropionic acid corresponds with Böttiger's diphenopropionic acid (Abstr., 1884, 55) in composition, but not in constitution, as the latter contains two hydroxyl-groups.

Phosphorus pentasulphide reacts in the cold with thiophenyl-hydroxypropionic acid according to the equation  $2C_9H_{10}SO_3 + PCl_5 = S_2Ph_2 + 2C_3H_4O_3 + 2HCl + PCl_3$ . When phosphorus trichloride or oxychloride dissolved in benzene is warmed with thiophenyl-hydroxypropionic acid, the product poured off from the phosphorous or phosphoric acid and evaporated on a water-bath, *dithiophenyl dilactylic acid*,  $C_{18}H_{18}S_2O_5$ , remains as a yellow syrup, which solidifies when strongly cooled. Its salts are amorphous, those of the alkalis being readily soluble, whilst the barium salt forms a yellow resin sparingly soluble in water. The free acid is slowly decomposed by water, with separation of mercaptan, which soon changes to phenyl bisulphide. Dithiophenyl dilactylic acid has the constitution



and is not directly related to Lovén's dithiodilactylic acid (Abstr., 1884, 1299).  
A. K. M.

**Dehydracetic Acid.** By W. H. PERKIN, jun. (*Ber.*, 18, 218—220).—Knorr (Abstr., 1884, 1368; this vol., p. 247) and Paal (this vol., p. 248) having shown that pyrotritaric and carbopyrotritaric acids are derivatives of furfuran, it occurred to the author that in its constitution dehydracetic acid might likewise be related to the above acids. Perkin and Bernhart (Abstr., 1884, 1121) previously proved the presence of one ketone-group, whilst attempts to detect a second such group gave negative results. It is further shown that dehydracetic acid is not a hydroxy-acid, as it yields no acetyl-derivative when heated with a large excess of acetic anhydride. From these results, it is concluded that the fourth oxygen-atom occurs in the same form as in furfuran, the most probable formula being



The methyl salt of dehydracetic acid is readily soluble in water, the solution having a distinctly acid reaction. When the alcoholic solution is treated with alcoholic sodium ethoxide, the sodium compound  $C_8H_6NaMeO_4$  separates. On acidifying a solution of this, and then extracting with ether, an oil is obtained which after a time partly solidifies; the crystals obtained melt at 85—90°, methyl dehydracetate melting at 90·5°.  
A. K. M.

**Syntheses of Thiophen.** By V. MEYER (*Ber.*, 18, 217—218).—When ethyl sulphide is passed through a red-hot tube, a liquid is obtained which gives a splendid indophenin reaction, but the amount of thiophen produced has not been determined. Similar results are obtained when ethylene, coal-gas, or petroleum vapour is passed over heated pyrites. Thiophen is also produced when crotonic acid is heated with phosphorus sulphide, also by the action of the latter substance on normal butyric and on ordinary valeric acids, whilst not

a trace of thiophen is formed if isobutyric acid be employed. Finally thiophen is produced on boiling paraldehyde with phosphorus sulphide, or by heating this with ether at 300°. Owing to the small yield, the above reactions throw no light on the structure of thiophen.

A. K. M.

**Synthesis of Thiophen and Pyrroline Derivatives.** By C. PAAL (*Ber.*, 18, 367—371).—*Phenylmethylthiophen*,  $C_4SH_2MePh$  [Me : Ph = 2 : 5] is obtained by heating acetonephenoneacetone with phosphoric sulphide in sealed tubes for about half an hour at 120—130°. It crystallises in colourless needles, melts at 51°, boils at 270—272° (uncorr.), but sublimes even below 100°. It is readily soluble in ether, alcohol, chloroform, &c. When heated with sulphuric acid and a small quantity of isatine, it gives the blue coloration characteristic of the thiophens.

*Phenylmethylpyrroline*,  $C_4NH_3MePh$ , is obtained by heating acetonephenoneacetone with alcoholic ammonia for one hour in sealed tubes at 150°. It forms lustrous white plates, melts at 101°, sublimes readily in satiny plates; the vapours impart a red coloration to pine-wood moistened with hydrochloric acid. It is readily soluble in ether, alcohol, chloroform, benzene, &c. A solution in glacial acetic acid gives a purple-red coloration with sulphuric acid and isatin. The *picrate* forms dark red crystalline nodules. The potassium derivative forms white flocks.

A. J. G.

**Formation of Hydrocarbons by the Reversal of Friedel and Craft's Reaction.** By O. JACOBSEN (*Ber.*, 18, 338—344).—Some time back the author observed that durenene was always formed in addition to isodurenene, by the action of methyl chloride and aluminium chloride on mesitylene of known purity, and considered its formation to be due to a reverse action, in which methyl chloride and metaxylene were formed, the metaxylene then reacting with methyl chloride in the usual manner, and so leading to the formation of durenene. This reverse action, leading to the formation of durenene and other homologues from hexamethylbenzene, had been previously noticed by Friedel and Crafts (*Trans.*, 1882, 116). The following conclusions are drawn from numerous experiments on the various methylated benzenes:—

By the action of hydrogen chloride on methylated benzenes in presence of aluminium chloride, the methyl-groups can be eliminated as methyl chloride, the hydrocarbons being thus converted into lower homologues.

As hydrogen chloride is formed by the reaction of aluminium chloride with such hydrocarbons, a similar though less ready and complete reaction occurs when aluminium chloride and the hydrocarbons act on one another at suitable temperatures.

The methyl chloride formed in these reactions will be in part employed in the further methylation of the hydrocarbons present. In the more highly methylated hydrocarbons thus formed, a substitution of hydrogen for methyl may again occur, so that from the original hydrocarbons there may be formed indirectly homologues such as

could not be derived by the direct introduction of methyl-groups. In like manner, a polymethylated benzene may be converted into an isomeride (for instance mesitylene into pseudocumene).

In general, a higher temperature is more favourable to the elimination of methyl-groups by hydrogen chloride than to their introduction by means of methyl chloride. The elimination of methyl-groups occurs more readily with the higher methylated benzenes than with their lower homologues.

The author is now investigating this reaction in the case of benzene hydrocarbons having long side-chains. Ethylbenzene readily yields benzene when heated with aluminium chloride and hydrogen chloride at 130°.

A. J. G.

**Action of Amyl Chlorides and Amylene on Toluene.** By J. C. ESSNER and E. GOSSIN (*Bull. Soc. Chim.*, **42**, 213—216).—Amylene and both active and inactive amyl chloride act with great facility on toluene in presence of aluminium chloride. Liquid amyl toluenes are the products of the reaction. Active amyl chloride furnishes two amyltoluenes. The one boiling at 200—205° yields isophthalic acid with traces of phthalic acid when oxidised; the other, which constitutes the sole product of the reactions with inactive amyl chloride and with amylene, is a colourless liquid boiling at 208°, having a camphoraceous odour and a sp. gr. of 0·8679 at 22°. When oxidised at 100° with potassium permanganate, it yields isophthalic acid, together with a small quantity of terephthalic acid and traces of phthalic acid. When this amyl toluene is brominated, an uncrystallisable liquid is obtained, which appears to be a mixture of bromoderivatives. The hydrocarbon is not dissolved by ordinary sulphuric acid, but is soluble in the fuming acid. Fuming nitric acid causes an intense blue coloration, which is discharged on the addition of water, whilst the action of a mixture of nitric and sulphuric acids gives rise to the formation of a yellow liquid nitro-derivative.

The reaction with amylene does not result in the formation of hydrogen chloride, and probably consists in the direct union of the two hydrocarbons. In the case of the two amyl chlorides, the result is most simply explained by the supposition that amylene is first formed from the chlorides with evolution of hydrogen chloride, and that the unsaturated hydrocarbon then combines with the toluene,  $C_5H_{11}Cl = C_5H_{10} + HCl$ ;  $C_5H_{10} + C_7H_8 = C_7H_7(C_5H_{11})$ . Active amyl chloride decomposes in this way with the direct production of tertiary isoamyltoluene; the inactive chloride yields the same hydrocarbon by a similar reaction, accompanied by molecular transformation. The constitution of this hydrocarbon is therefore *di-methylethylmetatolylmethane*.

W. R. D.

**Action of Chloropicrin and Chloroform on Toluene in Presence of Aluminium Chloride.** By K. ELBS and O. WITTICH (*Ber.*, **18**, 347—349).—A continuation of Elbs' synthesis by means of chloropicrin (*Abstr.*, 1883, 1000). By the reaction of chloropicrin and toluene, diluted with carbon bisulphide, there are obtained ditolylmethane, tritolylmethane, and a clear yellow oil of high boiling point,

and of the formula  $C_{22}H_{22}$ , in all probability a mixture of isomeric substances. By the action of chloroform on toluene in presence of aluminium chloride, Schwartz obtained amongst other products a substance which he regarded as tetratolyethane. The authors, on repeating the experiment, have obtained what appears to be the same substance, but from its chemical behaviour they consider that it must be looked on as a *dimethylanthracene*. It melts at  $215-216^\circ$ , and when oxidised yields a quinone that forms nearly colourless needles, and melts at  $161-162^\circ$ . This dimethylanthracene differs, therefore, from the two described respectively by Van Dorp (this Journal, 1872, 1006), and by Zincke and Wachendorff (*Ber.*, 10, 1482). A. J. G.

**Benzene  $\beta$ -Hexachloride.** By J. MEUNIER (*Compt. rend.*, 100, 358—360).—The isomeride of benzene hexachloride previously described (*Abstr.*, 1884, 733; and this vol., p. 52) is decomposed by boiling alcoholic potash, with formation of potassium chloride and liquid trichlorobenzene, identical with that obtained by the action of chlorine on benzene in presence of iodine. Decomposition is only complete after boiling for three or four hours, whilst ordinary benzene hexachloride is completely decomposed in an hour.

The author criticises some of Schüpphaus's observations (this vol., p. 52), and maintains that the crystals of the isomeride are optically inactive. The double refraction observed by Schüpphaus was probably due to the presence of the ordinary hexachloride, which can only be removed by careful fractional sublimation. C. H. B.

**Influence of Light on the Course of Chemical Reactions in the Bromination of Aromatic Compounds.** By J. SCHRAMM (*Ber.*, 18, 350—355).—Bromine has no action on parabromotoluene in the dark at ordinary temperatures, but on exposure to light, converts it into parabromobenzyl bromide; the rapidity of the reaction is directly as the intensity of the light. On ethyl benzene also, bromine has no action in the dark; on exposure to the light,  $\alpha$ -phenylbromethane,  $CHBrMePh$ , is formed. The further bromination of this compound has considerable interest, inasmuch as different products are obtained under different conditions. When a mixture of  $\alpha$ -phenylbromethane with bromine (1 mol.), or of ethylbenzene with bromine (2 mols.), is exposed to direct sunlight at the ordinary temperature, phenylbromacetole,  $CBr_2MePh$ , is formed; whilst if the mixtures are exposed to diffused daylight, the reaction is very slow, and the isomeric cinnamene dibromide,  $CHBrPh.CH_2Br$ , is obtained. The latter substance is also formed on heating a mixture of  $\alpha$ -phenylbromethane and bromine (1 mol.) on the water-bath, daylight being excluded. The introduction of a third bromine-atom into phenylbromacetole can only be effected under the conjoint action of heat and direct sunlight. A. J. G.

**Bromosubstitution-derivatives of Metaxylene.** By O. JACOBSEN (*Ber.*, 18, 356—359).—The discrepancy between the author's and Jannasch's determinations of the melting point of monobromoparaxylene (*Annalen*, 151, 238; this Journal, 1874, 468; this vol., 144 and

251) are explained by the substance showing in a high degree the property of superfusion. Samples of known purity were cooled to  $-10^{\circ}$  to  $-15^{\circ}$  without solidifying; but on exposure to the cold of a winter's night (minimum temperature  $-12^{\circ}$ ) solidified to a crystalline mass. The addition of a crystal to other cooled samples at once started crystallisation. The melting point was found to be  $8.9^{\circ}$ , thus agreeing well with Jannasch's determination.

A liquid dibromopara-xylene was obtained in small quantity; it boils at  $260-264^{\circ}$ , and solidifies in a freezing mixture. A tribromo-derivative could not be obtained. Tetrabromopara-xylene crystallises in slender needles, melts at  $253^{\circ}$ , and boils at about  $355^{\circ}$ ; it is very sparingly soluble in hot alcohol. A. J. G.

**Perchlorophenol from Perchlorobenzene.** By A. WEBER and N. WOLFF (*Ber.*, 18, 335—337).—Perchlorobenzene is partially converted into perchlorophenol by heating with alcoholic soda in sealed tubes at  $150-160^{\circ}$ . A much better yield is obtained by heating with caustic soda and anhydrous glycerol in sealed tubes at  $250-280^{\circ}$ .

A. J. G.

**Paranitrophenyl Mercaptan and Paranitrophenyl Disulphide.** By C. WILLGERODT (*Ber.*, 18, 331—333).—*Paranitrophenyl mercaptan*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SH}$ , is obtained by heating paranitrochlorobenzene with an aqueo-alcoholic solution of potassium sulphide, and decomposing the potassium mercaptide formed by means of hydrochloric acid. It is crystalline, melts at  $77^{\circ}$ , is readily soluble in water and alcohol on heating, and in ether, chloroform, and acetone in the cold; it is sparingly soluble in glacial acetic acid and light petroleum. It is oxidised very readily on exposure to air. Titrated with potassium permanganate in acid solution, it takes up 1 atom of oxygen per molecule, and yields a white compound melting at  $180-181^{\circ}$ . It dissolves in alkalis or alkaline earths, yielding yellow solutions of the corresponding mercaptides. These solutions give precipitates with most metallic salts. The silver mercaptide is grey, the lead salt orange, the copper salt greenish-yellow, and the nickel salt a fine brownish-red.

*Paranitrophenyl disulphide*,  $(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2\text{S}_2$ , obtained in the preparation of the mercaptan, crystallises in short colourless prisms, melts at  $181^{\circ}$ , and is soluble in alcohol. A. J. G.

**$\alpha$ -Dinitrophenyl Thiobenzoate and the Ethers of Dinitrophenylmercaptan.** By C. WILLGERODT (*Ber.*, 18, 328—331).—*Dinitrophenylthiobenzoate*,  $\text{Bz}\cdot\text{S}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$  [ $\text{NO}_2 : \text{NO}_2 = 2 : 4$ ], is prepared by the successive action of potassium sulphide and benzoic chloride on  $\alpha$ -dinitrochlorobenzene. It crystallises in long, nearly colourless needles, melts at  $113^{\circ}$ , is insoluble in cold water, sparingly soluble in boiling light petroleum or glacial acetic acid, more soluble in hot alcohol, very readily soluble in ether, chloroform, acetone, and benzene. When heated with alkalis, it is decomposed into benzoic acid and dinitrophenylmercaptan. By the action of nitric acid, it is converted into a crystalline sulphonic acid.

The ethers of dinitrophenylmercaptan are prepared by the action of



the alkyl haloïds on alcoholic solutions of the mercaptides of the alkali-metals. They are all readily soluble in ether, chloroform, benzene, acetone, and ethyl acetate, more sparingly soluble in alcohol, glacial acetic acid, and light petroleum. *α-Dinitrophenyl ethyl thioether* crystallises in yellow needles and melts at 113°. Nitric acid oxidises it to a substance forming small white crystals melting at 156—158°. The *methyl ether* forms small yellow crystals and melts at 126°. The *isopropyl ether* crystallises in thick yellow prisms and melts at 93—94°. The *isobutyl ether* crystallises in nodules and melts at 71—72°. The *benzyl ether* forms yellowish rhombic plates and melts at 128°.

A. J. G.

**Substances Formed by the Fusion of Quinol with Soda.** By J. BARTH and L. SCHREDER (*Monatsh. Chem.*, 5, 589—604).—The authors have already shown that this reaction yields hydroxyquinol (Abstr., 1883, 987); the present paper deals with other substances formed at the same time. The fusion and treatment of the fused mass with dilute sulphuric acid and repeated extraction with ether have been already described (*loc. cit.*). The first four ethereal extracts are evaporated, the residue dissolved in water, filtered, a little lead acetate added to the filtrate, and the slimy precipitate formed filtered off; to the filtrate, lead acetate (with sufficient basic lead acetate to ensure the liquid being only slightly acid) is added, when a voluminous precipitate of the lead salts of hydroxyquinol and of *δ*-hexahydroxydiphenyl is obtained, whilst the filtrate contains diquinol; this is separated in the manner previously described. The lead salts are decomposed by hydrogen sulphide, the filtrate from the lead sulphide is extracted with ether, and the residue from the ethereal extract mixed with the residues from the fifth to twelfth ethereal extracts of the original acid solution. The purification of this mixture is then effected by crystallisation from amyl alcohol, solution in ether, and treatment with animal charcoal; finally the residue from the ethereal solution is submitted to fractional crystallisation from water, when hexahydroxydiphenyl crystallises first.

*Hydroxyquinol*,  $C_6H_3(OH)_3$ , when pure melts at 140·5° (uncorr.). It crystallises in the monoclinic system; axial ratios  $a : b : c = 0·75 : 1 : 1·01$ ;  $\eta = 91·46^\circ$ ; observed forms 001, 110,  $\bar{1}11$ . The acetyl-derivative,  $C_6H_3O_3\bar{A}c_3$ , forms tufts of white needles, stable in air, and melts at 96·5°. Bromine converts hydroxyquinol into tribromhydroxyquinone,  $C_6HBr_3O_3$ ; this crystallises in orange-red forms and melts at 206—207°. Sulphuric acid dissolves hydroxyquinol in the cold, forming a dark-green solution, which gradually changes to violet; when heated on the water-bath, the colour changes to dark cherry-red. *Hydroxyquinhydrone*,  $C_{12}H_{10}O_6$ , is formed by the careful addition of nitric acid to a solution of hydroxyquinol in water. It forms feebly lustrous dark greyish-blue crystals.

*δ-Hexahydroxydiphenyl*,  $C_{12}H_{10}O_6$ , forms nearly colourless tabular crystals resembling those of naphthalene; when moist, it absorbs oxygen with great eagerness from the air, turning first blue, and finally nearly black. It gives a blood-red coloration with alkalis, and a red coloration with ferric chloride. The acetyl-derivative crystallises in long white needles and melts at 172°.

Diquinol,  $C_{12}H_{10}O_4$ , crystallises in colourless plates, melts at  $237^{\circ}$  (uncorr.), and is readily soluble in ether and alcohol, more sparingly in water. When ferric chloride is added cautiously to its aqueous solution, the liquid turns red, and *diquinhydrone*,  $C_{12}H_8O_4$  or  $C_{24}H_{16}O_8$ , separates in slender violet needles with greenish lustre. They are readily soluble in alcohol and ether, nearly insoluble in water. *Diquinone*,  $C_{12}H_6O_9$ , can be obtained by the further action of ferric chloride on diquinhydrone, but it is better obtained by adding excess of ferric chloride to a hot boiling solution of diquinol. It crystallises in hair-like, straw-coloured needles, and melts, with incipient decomposition, at  $186-187^{\circ}$ .

A. J. G.

**Synthetical Researches in the Glucoside Group.** By A. MICHAEL (*Amer. Chem. J.*, **6**, 336—340; comp. Abstr., 1884, 439).—Synthetical methylarbutin after repeated crystallisation from water melts at the same temperature ( $174.5-175.5^{\circ}$ ) as the natural product. The identity of the two bodies is also shown by their behaviour towards polarised light; they also both crystallise at times from aqueous solutions in anhydrous crystals.

*Guaiacol glucoside* is obtained from the dried potassium derivative of guaiacol, by dissolving it in absolute alcohol with an equivalent weight of acetochlorhydroses. After remaining two or three days and filtering from potassium chloride, the solution on evaporation leaves the glucoside in fine white needles, ethyl acetate being at the same time given off. It is very soluble in hot water, and sparingly in alcohol and benzene. The crystals melt at  $156.5-157^{\circ}$ , and have a very bitter taste. The glucoside does not reduce silver nitrate or Fehling's solution even on boiling. It is decomposed by acids and alkalis into guaiacol and dextrose. The aqueous solution gives no coloration with ferric chloride.

*Eugenol glucoside* is obtained by the action of acetochlorhydroses on potassium eugenol. A mixture of the absolute alcoholic solutions of these bodies in equivalent proportions is allowed to remain a few days, and filtered from potassium chloride; on exposure to the air, the filtrate solidifies to clusters of needles. The crystals melt at  $132^{\circ}$ , and are readily soluble in hot water and alcohol, sparingly in hot benzene, and insoluble in cold benzene and ether. The aqueous solution reduces Fehling's solution on long boiling, but does not attack ammoniacal silver nitrate. Dilute acids convert it into eugenol and dextrose.

J. K. C.

**Direct Replacement of the Amido-group in Aromatic Amines by the Halogens.** By S. M. LOSANITSCH (*Ber.*, **18**, 39—41).—The author finds that when the aromatic amines are treated with a mixture of a halogen acid and nitric acid, a great part of the amine is converted into the halogen compound. Halogen substituted phenols and other halogen-derivatives are also amongst the products of decomposition. With hydrochloric and nitric acids, aniline yields chlorobenzene, chlorophenol, and a resinous product which is converted into chloranil when heated with aqua-regia. With hydrobromic and nitric acids, aniline yields bromobenzene, para-dibromo-

benzene, and orthobromophenol; hydriodic and nitric acids yield iodobenzene and iodophenol. With hydrochloric and nitric acids, ortho- and para-toluidine yield ortho- and para-chlorotoluene, but no chlorocresols were obtained; paranitraniline yields parachloronitrobenzene; tribromaniline yields bromotrichlorobenzene. With hydrobromic and nitric acids, tribromaniline gives tetrabromobenzene; and with hydriodic acid dibromodiodobenzene.

Aromatic hydrocarbons and other compounds can also be readily converted into halogen-derivatives by the help of these mixed acids.

L. T. T.

**Symmetrical Metaxylidine and Symmetrical Xylenol.** By A. THÖL (*Ber.*, **18**, 359—362).—*Nitrometatoluic acid*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{COOH}$ , is prepared by the oxidation of the nitroxylenes described by Wroblewski (*Abstr.*, 1881, 433). It forms crystalline nodules or colourless needles, melts at  $167^\circ$ , and is readily soluble in alcohol, ether, and hot water. The barium salt crystallises with 4 mols.  $\text{H}_2\text{O}$  in microscopic needles. As this acid differs from the three known nitrometatoluic acids, it follows that it must be the fourth possible acid of the constitution  $[\text{Me} : \text{COOH} : \text{NO}_2 = 1 : 3 : 5]$ . This was confirmed by reduction and conversion into the corresponding hydroxy-acid, when Jacobsen's symmetrical hydroxytoluic acid was obtained. From this result, it further follows that the metaxylidine and nitroxyldine described by Wroblewski (*loc. cit.*) are the symmetrical compounds. *Symmetrical metaxylenol*,  $\text{C}_6\text{H}_3\text{Me}_2\text{OH}$ , crystallises in slender white needles, melts at  $64^\circ$ , and boils at  $219.5^\circ$ . It does not give a coloration with ferric chloride. The *sodium* compound,  $\text{C}_6\text{H}_3\text{Me}_2\text{ONa}$ , crystallises in large colourless tables. The tribromo-derivative crystallises in slender interlaced needles and melts at  $162.5^\circ$ .

A. J. G.

**Pseudocumidine.** By S. HALLER (*Ber.*, **18**, 89—94).—The researches of Hofmann (*Abstr.*, 1883, 324) and of Liebermann and v. Kostanecki (*Abstr.*, 1884, 1146) seem to show that the commercial cumidine prepared from dimethylxyldine, is identical with Schaper's pseudocumidine (*Zeit. f. Chem.*, 1867, 13), and therefore has the constitution  $\text{C}_6\text{H}_2\text{Me}_3\text{NH}_2$   $[\text{NH}_2 : \text{Me}_3 = 1 : 2 : 4 : 5]$ . The present investigation of this commercial cumidine was undertaken to confirm these results.

Diazocumidine sulphate was treated with alcohol in order to obtain the corresponding cumene. Instead of this, the ethyl ether of pseudocumenol,  $\text{C}_6\text{H}_2\text{Me}_3\text{OEt}$ , was formed. The hydrocarbon was, however, easily obtained by a method privately communicated to the author by Baeyer. This consists in treating the hydrazine with a solution of copper sulphate.

*Sodium diazo-pseudocumene sulphite*,  $\text{C}_6\text{H}_2\text{Me}_3\text{N}_2\text{SO}_3\text{Na} + 2\frac{1}{2}\text{H}_2\text{O}$ , was obtained by mixing solutions of the diazo-chloride and sodium sulphite. It is easily soluble in water and crystallises in yellow scales. When boiled with water or acids, it yields pseudocumenol. *Sodium pseudocumylhydrazine sulphite*,  $\text{C}_6\text{H}_2\text{Me}_3\text{N}_2\text{H}_2\text{SO}_3\text{Na} + 1\frac{1}{2}\text{H}_2\text{O}$ , was obtained by the reduction of the diazo-compound with zinc and acetic acid. It crystallises in glistening scales easily soluble in boiling water. It

reduces Fehling's and ammoniacal silver solutions, and decomposes at  $110^{\circ}$ . *Pseudocumylhydrazine*,  $C_6H_2Me_3.N_2H_3$ , crystallises in colourless needles melting at  $120^{\circ}$ . It is easily soluble in alcohol, ether, and chloroform, very sparingly in water and alkalis. Its *hydrochloride* crystallises in yellowish needles. The hydrazine was boiled with four times its weight of water, and a 10 per cent. solution of copper sulphate allowed to drop in. Each drop produced a reddish-brown precipitate, which quickly decomposed, nitrogen being evolved, and cuprous oxide and a brown oil being produced. This oil, when purified, boiled at  $169-170^{\circ}$ , and the author established its identity with pseudocumene by preparing from it the characteristic monochloro-, monobromo-, and trinitro-derivatives, durylonitrile, and durylic acid. It is thus clear that the commercial cumidine in question is identical with pseudocumidine. L. T. T.

**Paramidoctylbenzene, Paramidocaprylbenzene, and Amidooctyltoluene.** By A. BERAN (*Ber.*, 18, 131—149). *Paramidoctylbenzene*,  $C_8H_{17}.C_6H_4.NH_2$ , is obtained on heating normal octyl alcohol (7 grams) with 25 grams aniline zinc chloride (2 mols. aniline to 1 mol. zinc chloride) for about eight hours at  $270-280^{\circ}$ . The product is treated with warm dilute hydrochloric acid, an excess of ammonia added, and the mixture when cold extracted with ether; the ether is then distilled off and the oil fractionated. The fraction  $300-320^{\circ}$  is treated with dilute sulphuric acid, the precipitated sulphate well washed with water, treated with boiling alcohol, and decomposed by means of soda solution. Amidooctylbenzene boils at  $310-311^{\circ}$ , is colourless and odourless when freshly distilled, but becomes coloured by exposure to air. When cooled it solidifies to large colourless plates melting at  $19.5^{\circ}$ . It is moderately volatile in steam. The *hydrochloride*,  $C_{14}H_{23}N.HCl$ , *sulphate*,  $(C_{14}H_{23}N)_2.H_2SO_4$ , and *oxalate*,  $(C_{14}H_{23}N)_2.H_2C_2O_4$ , are well characterised salts.

*Formylphenooctylamine (formylamidooctylbenzene),*



obtained by the action of formic acid on amidooctylbenzene, forms large white lustrous scales melting at  $56^{\circ}$ , is almost insoluble in warm water, but readily soluble in warm alcohol and ether. *Acetylphenooctylamine*,  $C_8H_{17}.C_6H_4.NHAc$ , obtained from amidooctylbenzene and acetic anhydride, forms large colourless scales or plates melting at  $93^{\circ}$ , it is insoluble in water, readily soluble in alcohol, ether, and light petroleum. *Benzoylphenooctylamine*,  $C_8H_{17}.C_6H_4.NHBz$ , is prepared from amidooctylbenzene and benzoic chloride. It forms large white lustrous scales, melts at  $117^{\circ}$ , is insoluble in hot water, but dissolves readily in warm alcohol and ether; it may be heated with aqueous soda without decomposition. Amidooctylbenzene may be converted (by means of the diazo-reaction) into *paridoctylbenzene*,  $C_8H_{17}.C_6H_4I$ ; this is a heavy yellowish oil, which boils at  $318-320^{\circ}$ , and does not solidify in a freezing mixture; when oxidised by chromic acid, it yields paridobenzoic acid (m. p.  $266^{\circ}$ ), showing that amidooctylbenzene is a para-derivative. When formylphenooctylamine is distilled with zinc-dust, *octylbenzonitrile* is obtained (see Abstr., 1884, 734). This boils

at about  $312^{\circ}$ , and is converted by saponification into *parooctylbenzoic acid*,  $C_8H_{17}.C_6H_4.COOH$ , which melts at  $139^{\circ}$ .

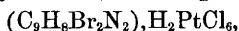
*Paramidocaprylbenzene* (*paraphencaprylamine*),  $C_8H_{17}.C_6H_4.NH_2$ , is obtained in the same way as the octyl-compound, and forms a colourless and odourless oil which boils at  $290-292^{\circ}$  (corr.), and does not solidify at  $-20^{\circ}$ . The *oxalate*,  $(C_{14}H_{23}N)_2.H_2C_2O_4$ , and *sulphate* are more soluble than the corresponding salts of amidoctylbenzene. The acetyl-derivative could not be obtained in the solid state, whilst the *benzoyl-derivative*,  $C_8H_{17}.C_6H_4.NHBz$ , forms slender white needles melting at  $109^{\circ}$ . *Pariodocaprylbenzene* is a yellow oily liquid boiling at  $304-305^{\circ}$ ; it yields pariodobenzoic acid on oxidation. Paramidoctylbenzene and paramidocaprylbenzene may also be obtained by heating octyl or capryl alcohol with aniline hydrochloride, but the yield is smaller than by the method above described.

*Amidoctyltoluene* (*tolocetylamine*),  $C_8H_{17}.C_6H_3Me.NH_2$ , is prepared by heating 8 grams normal octyl alcohol with 30 grams orthotoluidine zinc chloride for 7—8 hours at  $280^{\circ}$ . It is an odourless and colourless oil, boiling at  $324-326^{\circ}$ , and does not solidify at  $-20^{\circ}$ . The *hydrochloride*,  $C_{15}H_{25}N.HCl$ , *sulphate*,  $(C_{15}H_{25}N)_2.H_2S_2O_4$ , and *oxalate*,  $(C_{15}H_{25}N)_2.H_2C_2O_4$ , form well crystallised salts. *Acetyltoctylamine*,  $C_8H_{17}.C_7H_6.NHAc$ , forms slender white needles, melting at  $81^{\circ}$ , and readily soluble in warm alcohol and ether. *Benzoyltolocetylamine*,  $C_8H_{17}.C_7H_6.NHBz$ , crystallises in large white lustrous scales, melts at  $117^{\circ}$ , and dissolves readily in warm alcohol, sparingly in ether.

A. K. M.

**Action of Bromine on Propenylphenylenediamine.** By E. G. SMITH (*Amer. Chem. J.*, **6**, 172—178).—*Orthonitropropionanilide*,  $NO_2.C_6H_4.NH.COEt$  [1 : 2], is prepared by treating orthonitraniline (melting at  $71^{\circ}$ ) with propionic chloride; it is soluble in water, alcohol, ether, and benzene, and separates from its solutions in lemon-yellow scales, melting at  $63^{\circ}$ . Treated with reducing agents, it forms *propenylphenylenediamine*,  $C_6H_4.<\frac{N}{NH}>CEt$ , identical with that described by Wundt (*Abstr.*, 1878, 668). This base forms a series of well-defined salts, which crystallise without water of crystallisation. The *hydrochloride*,  $C_9H_{10}N_2.HCl$ , forms long colourless crystals; the *platinochloride*,  $(C_9H_{10}N_2)_2.H_2PtCl_6$ , forms bright orange-red crystals. The *mercurio-chloride*,  $(C_9H_{10}N_2)_2.H_2HgCl_4$ , crystallises in long colourless needles.

Bromine-water reacts on propenylphenylenediamine, forming a dibromo- and tribromo-derivative, and a small quantity of an acid which has not been investigated. *Propenyldibromophenylenediamine*,  $C_6H_2Br_2(N_2C_3H_6)$ , is sparingly soluble in water, but readily soluble in benzene, ether, dilute alcohol, and strong soda solution; it melts at  $224-226^{\circ}$ . The *nitrate* and *hydrochloride* of this base are soluble in water, and crystallise well; the *platinochloride*,



forms orange-red crystals.

*Propenyltribromophenylenediamine*,  $C_6HBr_3(N_2C_3H_6)$ , forms pale-yellow granular crystals, which are sparingly soluble in alcohol, ether,

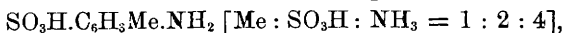
benzene, and hot water; it melts at 257—262°. Its *hydrochloride*,  $C_6H_7Br_3N_2.HCl + 2H_2O$ , forms small transparent crystals which are soluble in water.

P. P. B.

**Oxidation of Aromatic Amines.** By J. BARZILOVSKY (*J. Russ. Chem. Soc.*, 1885, 38).—This is a continuation of the author's work (Abstr., 1879, 237). In the present paper he states that the ruby-coloured azo-compound,  $C_{28}H_{26}N_4$ , obtained by him, and since examined by Klinger and Pitschke (this vol., p. 151), is a product of the oxidation of paratoluidine alone, and can be obtained by oxidising the salts of this base, whence he concludes that it cannot have the constitution  $C_{21}H_{17}(NH_2)_2.N_2C_7H_5$ , as suggested by Klinger and Pitschke, and in fact must contain less hydrogen than is required by this formula.

A. T.

**Action of Alcohol on Diazo-compounds.** By I. REMSEN (*Ber.*, 18, 65—66).—Referring to the recent communications of Hofmann, Hallen, and Wroblewski, the author calls attention to the fact that Brown (Abstr., 1883, 471) observed the introduction of the ethoxyl-group by the decomposition of a diazo-compound with alcohol, and that similar observations had previously been made by Hayduck (this Journal, 1874, 1094) and Zander (Abstr., 1880, 122). By treatment of the diazo-derivative of amidotoluenesulphonic acid,



with alcohol, Palmer has lately obtained a mixture of ethoxyltoluenesulphonic and toluene-sulphonic acids.

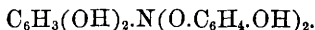
L. T. T.

**Diazo-compounds.** By K. GASIOROWSKI and A. WAÏSS (*Ber.*, 18, 337—338).—It has been shown by Effront (this vol., p. 152) that hydrocarbons are formed by the action of stannous salts on the chlorides of diazo-compounds. The authors are extending this reaction. The action of stannous formate on diazobenzene formate yields small quantities of benzene, diphenyl, and a nitrogenous explosive oil boiling at 165°. Larger quantities of benzene and diphenyl are obtained on substituting stannous chloride for the formate, whilst by using stannous chloride and hydrochloric acid, not inconsiderable quantities of chlorobenzene are formed. Diazobenzene chloride when heated in aqueous solution with excess of hydrochloric acid, yields phenol and chlorobenzene. Bromobenzene is similarly formed, but in larger quantity, by the action of an excess of hydrobromic acid on diazobenzene bromide.

A. J. G.

**Colouring Matters from Phenols.** By H. BRUNNER and W. ROBERT (*Ber.*, 18, 373—375).—In the preparation of nitroso-resorcinol, by the action of amyl nitrite on the monosodium derivative of the phenol, and subsequent precipitation with dilute sulphuric acid, it was found that after a time the wash-water deposited dark crusts of a mixture of two compounds, distinguished by the difference of their solubility in ether. The colouring matter soluble in ether,  $C_{18}H_{15}NO_6$ , forms a cantharadine-green mass, soluble in alkalis, with bluish-violet colour and reddish-brown fluorescence, in concentrated hydrochloric acid with red, and in concentrated sulphuric acid with blue colour. It appears

probable that it may be formed by condensation from 2 mols. of resorcinol and 1 mol. of nitroresorcinol, and have the formula



The substance insoluble in ether forms a brown mass, soluble in alkalis to a dirty violet liquid without fluorescence, and in sulphuric acid to a blue liquid. It could not be obtained sufficiently pure for analysis.

A. J. G.

**Resorcinol Dyes.** By P. WESELSKY and R. BENEDIKT (*Monatsh. Chem.*, **5**, 605—614).—A considerable portion of this paper is taken up with criticisms on Brunner and Cramer's work on this subject (Abstr., 1884, 1333). "Weselsky's resorcinol," when reduced in ammoniacal solution by means of zinc-dust or hydrogen sodium sulphite, yields diazoresorufin; a similar result is obtained by reduction with other alkaline reducing agents, or by an acid solution of ferrous chloride. "*Fluorescent resorcinol blue*" is prepared by adding bromine to a solution of "diazoresorcinol" in potassium carbonate, and precipitating with hydrochloric acid. It forms small needles of greenish lustre, very sparingly soluble in water or absolute alcohol, more soluble in dilute alcohol. The solution is blue, and shows a strong red fluorescence. In acid baths, it dyes silk and wool blue, with red fluorescence. A non-fluorescent blue is obtained by the action of bromine-water on a dilute alkaline solution of "diazoresorcinol." It forms green needles, and dissolves in alcohol or sulphuric acid to pure blue non-fluorescent liquids. It dyes silk and wool a very fine blue, but in the dyeing is very readily converted into the fluorescent blue, a change also readily effected by reducing agents, or by heating with sulphuric acid.

A. J. G.

**Conversion of Organic Isocyanates into Thiocarbimides.** By A. MICHAEL and G. M. PALMER (*Amer. Chem. J.*, **6**, 257--260).—Phenyl isocyanate and phosphorus pentasulphide were heated together at 160°, when phenylthiocarbimide was formed in almost theoretical quantity. This reaction appears to be a general one, as ethylthiocarbimide may be formed in a similar manner. By the action of phosphorus pentasulphide on phenylurethane, phenylthiocarbimide is formed.

H. B.

**Benzylarsines.** By A. MICHAELIS and U. PAETOW (*Ber.*, **18**, 41—45).—In continuation of the work of Michaelis in conjunction with other investigators (Abstr., 1882, 1062; 1883, 185, 327; 1884, 1135, 1180), the authors have studied the action of sodium on mixtures of benzyl and arsenious chlorides (in ethereal solution). The reaction is much slower than when chlorobenzene is employed; when arsenious chloride is in excess, no reaction takes place; when benzyl chloride preponderates, a good deal of dibenzyl is formed. If a mixture of 1 mol. arsenious chloride and 2 mols. benzyl chloride, diluted with four times its volume of ether, is treated with the calculated quantity of sodium, a very slow action takes place, *dibenzylarsine trichloride*,  $(\text{C}_7\text{H}_7)_2\text{AsCl}_3$ ,

and *tribenzylarsine dichloride* being formed, according to the equations  $2C_7H_7Cl + AsCl_3 + 2Na = (C_7H_7)_2AsCl_3 + 2NaCl$  and  $3C_7H_7Cl + AsCl_3 + 4Na = (C_7H_7)_3AsCl_2 + 4NaCl$ . If, however, after the addition of the sodium, a little pure ethyl acetate is added, a violent reaction at once sets in, so that the vessel must be well cooled. *Tribenzylarsine*,  $As(C_7H_7)_3$ , is then formed in addition to the above two, the proportion being greater the better the mixture is cooled during the reaction.

The product from the reaction without ethyl acetate was, after distilling off the ether, treated with wet ether. The arsine chlorides were oxidised and rendered insoluble in ether, whilst the resinous matter went into solution. The residue was then treated with dilute sodium hydroxide, when *dibenzylarsinic acid*,  $(C_7H_7)_2AsO.OH$ , was dissolved, and *tribenzylarsine oxide*,  $As(C_7H_7)_3O$ , left. *Dibenzylarsinic acid* forms white scales, sparingly soluble in ether, benzene, and cold water, more easily in boiling water. It melts at  $210.5^\circ$ , and when dissolved in boiling dilute hydrochloric acid, yields a *hydroxychloride* of the formula  $As(C_7H_7)_2(OH)_2Cl$ , which melts at  $128^\circ$ , and is reconverted into the acid by water. Strong hydrochloric acid decomposes the acid into arsenious acid, benzyl chloride, and, apparently, toluene. This acid, therefore, resembles cacodylic acid, and may be looked upon as a diphenyl-derivative of the latter. The alkaline and alkaline-earth salts are soluble, the silver salt insoluble. *Tribenzylarsine oxide* crystallises in needles melting at  $219.5^\circ$ . It is sparingly soluble in cold, more easily in boiling water and in alcohol; insoluble in hydrochloric acid. With hydrochloric acid, the aqueous solution yields a *hydroxychloride*,  $As(C_7H_7)_3Cl.OH$ , melting at  $162-163^\circ$ . *Tribenzylarsine* is soluble in alcohol and ether; it crystallises in flat colourless needles, and melts at  $104^\circ$ . With ethyl iodide, it yields *tribenzylethylarsonium iodide*,  $As(C_7H_7)_3EtI$ , crystallising in white scales. It also combines, but only very slowly even at  $200^\circ$ , with benzyl chloride. It is isomeric with paratritolylarsine, prepared by Michaelis and La Coste.

L. T. T.

**Action of Aldehyde on Paranitrobenzaldehyde.** By C. F. GÜHRING (*Ber.*, 18, 371—373).—Baeyer and Drewson have shown that orthonitro- $\beta$ -phenyllactic aldehyde is obtained by the action of orthonitrobenzaldehyde on acetaldehyde (*Abstr.*, 1884, 58). Substituting the paranitro- for the ortho-compound, under like conditions, the author has obtained a compound of aldehyde with *paranitro- $\beta$ -phenyllactic aldehyde*,  $NO_2.C_6H_4.CH(OH).CH_2.COOH$ ; this crystallises in colourless prisms, melts with decomposition at  $115^\circ$ , and is readily soluble in alcohol and ether. It is less readily decomposed than the ortho-compound. When oxidised with alkaline permanganate, it yields paranitrobenzoic acid; with silver oxide, on the other hand, it is oxidised to paranitro- $\beta$ -phenyllactic acid.

*Paranitrocinnamaldehyde*,  $NO_2.C_6H_4.CH : CH.CO.H$ , is obtained by heating paranitro- $\beta$ -phenyllactic aldehyde with acetic anhydride, or even by long-continued boiling with water. It forms long colourless needles, melts at  $135^\circ$ , shows the characteristic reactions of an aldehyde, and yields paranitrocinnamic acid when oxidised with silver oxide.

A. J. G.



**Compounds of Benzaldehyde with Aniline Hydrochloride and with Stannic Chloride.** By A. ELBERS (*Annalen*, **227**, 357—359).—When benzaldehyde is added to a solution of aniline in strong hydrochloric acid, a crystalline compound is deposited, which is freely soluble in hot concentrated hydrochloric acid, but is decomposed by the addition of water. A yellow precipitate is also thrown down when stannic chloride is added to a mixture of benzaldehyde with aniline in hydrochloric acid solution. This consists of a mixture of the preceding substance with a compound of 2 mols. aniline hydrochloride, 1 mol. stannic chloride, and 3 mols. benzaldehyde. This double salt is less soluble in strong hydrochloric acid than the preceding compound.

W. C. W.

**Actions of Sulphuric Acid on the Phenylcrotonic Acids.** By H. ERDMANN (*Annalen*, **227**, 247—261).—I. *Phenylmethacrylic acid*,  $\text{CHPh} : \text{CMe} \cdot \text{COOH}$ , is most easily prepared by heating a mixture of sodium propionate, dried at  $140^\circ$  (4 mols.), and benzalchloride (1 mol.) at  $150^\circ$  for 8—10 hours. The access of air to the flask in which the operation is conducted must be avoided as far as possible, in order to minimise the formation of benzoic acid.

Phenylmethacrylic acid is decomposed by prolonged boiling with sulphuric acid (60 c.c. of water to 40 c.c. acid), carbonic anhydride being evolved and a hydrocarbon, *methronene*, formed. To isolate this hydrocarbon, the acid mixture is neutralised with soda and extracted with ether. The residue, on evaporating the ether, is distilled in a current of steam. Methronene,  $\text{C}_{18}\text{H}_{20}$ , is a pale yellow-liquid. It boils at  $322^\circ$ , and has not been solidified. The vapour-density is 8.06 compared with that of air. Methronene yields a sulphonic acid and a nitro-derivative, neither of which were obtained in a state of purity. It does not form an additive product with bromine. On oxidation with sulphuric acid and potassium dichromate, it splits up into carbonic anhydride, anthraquinone, and acetic and benzoic acids; the chief product of the reaction, however, is the benzoylbenzoic acid,  $\text{C}_{14}\text{H}_{10}\text{O}_3$ , discovered by Zincke.

The author regards methronene as *phenyldimethyltetrahydronaphthalene*,  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CHPh} \cdot \text{CHMe} \\ -\text{CH}_2 \cdot \text{CHMe}- \end{array} >$ .

II. *Phenylisocrotonic acid*,  $\text{CHPh} : \text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$ , from phenylparaconic acid is converted into phenylbutyrolactone by the action of sulphuric acid. By the action of sulphuric acid on the lactone, an acid is produced which has the same composition as phenylisocrotonic acid. The new acid crystallises in needles which melt between  $175^\circ$  and  $172^\circ$ . It is sparingly soluble in carbon bisulphide, water, and ether, and forms a very soluble calcium salt. It does not unite directly with bromine, but dissolves in fuming hydrobromic acid.

W. C. W.

**Oil of Gaultheria.** By H. P. PETTIGREW (*Pharm. J. Trans.* [3], **14**, 972—973).—It has been shown (Abstr., 1884, 459) that oil of birch is pure methyl salicylate, and therefore differs from oil of gaultheria. Two different samples of the latter oil have now been

examined, the sp. gr. in both cases = 1.17), and were found to contain only 0.3 per cent. of terpene, in addition to the methyl salicylate.

D. A. L.

**Derivatives of Hydratropic Acid. Artificial Formation of Phloretic Acid.** By P. TRINIUS (*Annalen*, **227**, 262—277).—On treatment with fuming nitric acid, hydratropic acid yields a mixture of ortho- and para-nitrohydratropic acids. The acids may be separated by means of their barium salts. On concentrating the aqueous solution, barium paranitrohydratropate crystallises out; the filtrate is evaporated to dryness, the residue powdered, dried over sulphuric acid, and treated with absolute alcohol, which dissolves out the barium salt of the ortho-acid.

*Paranitrohydratropic acid*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{COOH}$ , is deposited as an oily liquid when hydrochloric acid is added to the barium salt. The acid soon solidifies to a white crystalline mass melting at  $87^\circ$ . It is soluble in hot water, alcohol, benzene, and carbon bisulphide. The *barium salt*,  $(\text{C}_6\text{H}_5\text{NO}_2)_2\text{Ba} + 2\text{H}_2\text{O}$ , and the *calcium salt*,  $(\text{C}_6\text{H}_5\text{NO}_2)_2\text{Ca} + 2\text{H}_2\text{O}$ , are soluble in hot water but insoluble in absolute alcohol. When oxidised, paranitrohydratropic acid yields paranitrobenzoic acid.

*Paramidohydratropic acid*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{COOH}$ , prepared by reducing the nitro-acid with tin and hydrochloric acid, crystallises in thick plates melting at  $128^\circ$ . It is soluble in alcohol, ether, carbon bisulphide, and water. The compounds of this acid with bases easily decompose, but its compounds with acids are much more stable. The *hydrochloride*,  $\text{C}_6\text{H}_{11}\text{NO}_2\cdot\text{HCl}$ , is very soluble in water.

When a solution of this salt is treated with potassium nitrite, it is converted into *parahydroxyhydratropic acid*,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{COOH}$ , which is identical with phloretic acid in every respect, with the exception that it does not give a green coloration with ferric chloride. This reaction is probably due to the presence of phloroglucinol in the phloretic acid. Rochleder's (*Zeit. f. Chem.*, 1868, 711) isophloretic acid was in all probability pure parahydroxyhydratropic acid.

*Orthonitrohydratropic acid*,  $\text{C}_6\text{H}_5\text{NO}_2$ , forms colourless crystals melting at  $110^\circ$ . It is soluble in hot water, ether, and alcohol. The salts of the acid decompose when boiled with water. The *calcium salt*,  $(\text{C}_6\text{H}_5\text{NO}_2)_2\text{Ca} + 2\text{H}_2\text{O}$ , dissolves in water and in absolute alcohol. It crystallises in needles.

On oxidation, orthonitrohydratropic acid yields orthonitrobenzoic acid.

*Atroxindole*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{NH} \\ \text{CHMe} \end{smallmatrix}\rangle\text{CO}$ , is formed when granulated tin is added in small quantities at a time to a well-cooled mixture of orthonitrohydratropic and hydrochloric acids. Atroxindole melts at  $119^\circ$ , but begins to sublime at  $100^\circ$ . It dissolves in alcohol, ether, hydrochloric acid, and hot water, but is slightly decomposed by prolonged boiling with water. It appears to form compounds with alkalis. Atroxindole is isomeric with hydrocarbostyryl. If the reduction of orthonitrohydratropic acid is not carried on at a temperature of about zero, only a small quantity of atroxindole is produced, and the chief product is a substance which melts at  $195^\circ$ , and is almost insoluble in

hot dilute hydrochloric acid. Atroxindole is not attacked by tin and hydrochloric acid. W. C. W.

**Derivatives of Bromanisic Acid.** By L. BALBIANO (*Gazzetta*, 14, 234—251).—By the nitration of bromanisic acid there are produced a mono- and di-nitroanisoi, the former of which crystallises in white needles melting at 105°, described previously by Staedel, the latter in yellowish needles melting at 47°, soluble in alcohol and ether, insoluble in water, and converted into Laurent's dinitro-bromophenol by protracted boiling with a concentrated solution of sodium carbonate. As this dinitro-derivative is obtained by the nitration of the 1:2 bromophenol, the bromine and the methoxyl-group are in contiguous positions; the readiness with which the dinitro-bromanisoi is saponified would seem to indicate the correctness of Körner's formula  $C_6H_2Br(NO_2)_2.OH$  [ $OH:Br:NO_2:NO_2=1:2:4:6$ ], and a similar constitution for the anisoi or corresponding methoxy-derivative. Thus the constitution of the bromanisic acid is probably expressed by the formula



from which the mononitrobromanisoi is producible by the replacement of the carboxylic by the nitro-group.

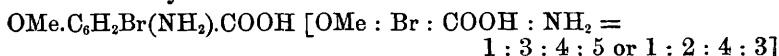
*Bromonitroanisic acid*,  $OMe.C_6H_2Br(NO_2).COOH$ , obtained as one of the products of the nitration of bromanisic acid, and separated from the above-mentioned compound by its solubility in ammonium carbonate, crystallises in glistening white needles, melting at 182°, insoluble in water, soluble in boiling alcohol. Its *potassium*, *sodium*, *calcium*, and *ammonium* salts crystallise in yellowish-white needles, its *silver* salt in stellate groups of white needles, its copper salt forms a sky-blue precipitate. The *ethyl* salt also crystallises in interlaced white needles melting at 85°. By reduction with ammonium sulphide, the nitro-acid is converted into the corresponding *amido-acid*,  $OMe.C_6H_2Br(NH_2).COOH$ , which crystallises in white needles melting at 185°, sparingly soluble in water, soluble in ether and alcohol; its hydrochloride crystallises in tufts of needles melting at 186°, sparingly soluble in alcohol and ether. The *calcium* salt crystallises in white needles, containing  $5\frac{1}{2}$  mols.  $H_2O$ , the barium salt with  $3\frac{1}{2}$  mols.  $H_2O$ ; the *zinc*, *copper*, and *silver* salts are insoluble precipitates. By reduction with zinc and hydrochloric acid, brom-amidoanisic acid is converted into the *amidoanisic acid*,



isomeric with the acid obtained by Zinin and others by the direct reduction of nitroanisic acid. The former crystallises in white needles melting at 204°, sparingly soluble in cold water; its *calcium* and *silver* salts are sparingly soluble precipitates; its platinumchloride forms yellowish grouped prisms, readily decomposed with separation of platinum. It is probable, inasmuch as it has been shown that in Zinin's amido-anisic acid the amido- and methoxy-groupings are in contiguous positions, that the constitution of the above acid is expressible by the formula

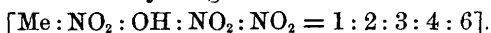


and that the brominated acid from which it is derived can be represented either by the formula



The author proposes to carry on further investigations to decide between the two possible formulæ. V. H. V.

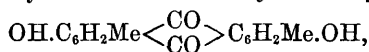
**Synthesis of Nitrococcusic Acid.** By S. v. KOSTANECKI and S. NIEMENTOWSKI (*Ber.*, **18**, 250—255).—Nitrococcusic acid was shown by Liebermann and v. Dorp to be a trinitrocresotic acid (this Journal, 1871, 913). Nölting and Salis (*Abstr.*, 1883, 59) found that of the three isomeric cresols, the meta-compound alone yields a trinitro-derivative, and to this they assigned the constitution



Assuming that the trinitrocresol from nitrococcusic acid is identical with Nölting and Salis's trinitrocresol (which the authors prove to be the case, see below), there remains only one position [5] for the carboxyl-group in nitrococcusic acid. Silver oxide dissolves in a boiling solution of the acid with evolution of carbonic anhydride as stated by De la Rue, but the product is found to be the silver derivative of trinitrocresol,  $\text{C}_6\text{HMe}(\text{NO}_2)_3.\text{OAg}$ . This trinitrocresol agrees with that of Nölting and Salis, not only in its melting point ( $106^\circ$ ) but also in yielding a naphthalene compound melting at  $126$ — $127^\circ$ , so that there is no doubt that the two are identical.

Nitrococcusic acid is obtained by the nitration of symmetrical hydroxytoluic acid. The identity of the product is confirmed by its composition, solubility, behaviour on heating, properties of its barium salt, and by its yielding a trinitrocresol when heated with water at  $180^\circ$ . This melts at  $106^\circ$ , yields the characteristic silver salt crystallising in yellow prisms, and the naphthalene compound melting at  $126$ — $127^\circ$ . The property possessed by nitrococcusic acid of readily yielding carbonic anhydride when boiled with silver oxide appears to be due to the presence of nitro-groups, as the metahydroxymetatoluic acid is only slightly decomposed by the same treatment.

Concentrated sulphuric acid reacts with symmetrical hydroxytoluic acid in the same way as with metahydroxybenzoic acid. The product may be separated into two portions by the action of baryta-water. The insoluble portion, corresponding to anthrarufin, yields a red fluorescent solution with concentrated sulphuric acid, the spectrum of which is almost coincident with that of anthrarufin; the alkaline solutions are golden-yellow. This *dimethylanthrarufin*,



forms yellow, silky needles melting at  $300^\circ$ . The portion soluble in baryta-water appears to contain two isomeric substances, which, however, have not yet been examined. A. K. M.

**Phenoxy-mucobromic Acid.** By H. B. HILL and E. K. STEVENS (*Amer. Chem. J.*, **6**, 187—194).—The formation of this acid from

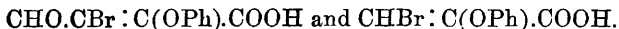
potassium phenate and mucobromic acid has been already described by one of the authors (Abstr., 1884, 731). It is most advantageously obtained by adding mucobromic acid to a solution of phenol dissolved in an excess of potassium hydroxide; in a short time crystals of the potassium salt of the new acid separate out, and are collected on a filter and subsequently decomposed by hydrochloric acid.

*Phenoxy-mucobromic acid*,  $\text{PhO.C}_4\text{H}_2\text{BrO}_3$ , so obtained, forms small, flat, concentrically grouped prisms; it melts at  $104\text{--}105^\circ$ , and is readily soluble in hot water, alcohol, or ether, and soluble in hot benzene or chloroform, but almost insoluble in carbon bisulphide or light petroleum. The aqueous solution of the acid reduces silver oxide on warming, and gives a white precipitate with ferric chloride. The potassium salt,  $\text{PhO.C}_4\text{HBrO}_3\text{K}$ , forms oblique tabular crystals soluble in cold water; the barium salt,  $(\text{PhO.C}_4\text{HBrO}_3)_2\text{Ba} + 3\text{H}_2\text{O}$ , crystallises in easily soluble leafy rhombic crystals. Phenoxy-mucobromic acid, like mucobromic acid (*loc. cit.*), is decomposed by alkalis, and yields a corresponding acrylic acid.

*Phenoxybromoacrylic acid*,  $\text{PhO.C}_3\text{H}_2\text{BrO}_2$ , is obtained from its potassium salt, which, together with potassium formate, results from the decomposition of potassium phenoxy-mucobromate by potassium hydroxide. It crystallises from hot water in long silky needles melting at  $138^\circ$ , is sparingly soluble in hot water, very readily soluble in ether or alcohol, and soluble in warm chloroform or benzene. The potassium salt,  $\text{PhO.C}_3\text{HBrO}_2\text{K}$ , crystallises in rhombic plates; the barium salt,  $(\text{PhO.C}_3\text{HBrO}_2)_2\text{Ba} + 5\text{H}_2\text{O}$ , forms groups of radiating prisms, and the calcium salt also crystallises with  $5\text{H}_2\text{O}$  in clusters of needles. The silver salt,  $\text{PhO.C}_3\text{HBrO}_2\text{Ag}$ , crystallises in needles, dissolving in warm water without decomposition. Phenoxybromoacrylic acid is not attacked by alkalis.

*Phenoxybromomaleic acid*,  $\text{PhO.C}_4\text{H}_2\text{BrO}_4$ , is obtained when a solution of phenoxy-mucobromic acid is warmed with silver oxide. It crystallises in the form of fine felted needles melting at  $103\text{--}104^\circ$ . The silver salt,  $\text{PhO.C}_4\text{BrO}_4\text{Ag}_2$ , forms clusters of rhombic plates soluble in hot water.

The author regards the constitution of phenoxy-mucobromic and phenoxybromoacrylic acids as expressed by the following formulæ:—



P. P. B.

**Action of Potassium Cyanide on Phthalide.** By W. WISLICENUS (*Ber.*, 18, 172—174).—A mixture of potassium cyanide and phthalide is heated for three or four hours at  $180\text{--}185^\circ$ , and the product when cold is dissolved in a little cold water. Acid is then added in sufficient quantity to produce a permanent coloration, the impurities filtered off, and the filtrate treated with an excess of acid which throws down *benzylecyanideorthocarboxylic acid*,  $\text{COOH.C}_6\text{H}_4\text{CH}_2\text{CN}$ , as a bright yellow powder. It is insoluble in water, but very readily soluble in alcohol, ether, benzene, and chloroform, and melts at  $116^\circ$ . The silver, barium, and calcium salts,  $(\text{C}_6\text{H}_5\text{O}_2\text{N})_2\text{Ca} + 2\text{H}_2\text{O}$ , are described. When the acid is boiled with an excess of dilute potash, ammonia is evolved and *phenylacetorthocarboxylic acid*,

$\text{COOH.C}_6\text{H}_4.\text{CH}_2.\text{COOH}$ , is obtained. This dissolves readily in alcohol and hot water, more sparingly in cold water and ether, and is insoluble in benzene and chloroform; it melts at  $173.5^\circ$  with separation of water, and suffers complete decomposition at higher temperatures. The silver salt,  $\text{C}_9\text{H}_6\text{O}_4\text{Ag}_2$ , calcium salt,  $\text{C}_9\text{H}_6\text{O}_4\text{Ca} + 2\text{H}_2\text{O}$ , and barium salt,  $\text{C}_9\text{H}_6\text{O}_4\text{Ba}$ , are described. When the calcium salt is heated with soda-lime, toluene is obtained. The anhydride,  $\text{C}_9\text{H}_6\text{O}_3$ , is readily obtained by the action of acetic chloride on phenylacetorthocarboxylic acid, according to Anschütz's method (this vol., p. 243). It dissolves readily in ether and in chloroform, and crystallises from benzene in long prisms melting at  $140.5\text{--}141^\circ$ . A. K. M.

**Hydrindonaphthenecarboxylic Acid.** By E. SCHERKS (*Ber.*, 18, 378—383).—This acid was obtained by Baeyer and Perkin by the dry distillation of the dicarboxylic acid prepared by the action of ethylic sodomalonate on orthoxylene bromide (*Abstr.*, 1884, 752). It can be more economically prepared by acting on ethylic sodacetate with ortho-xylene bromide, and saponifying the product with alcoholic potash. By oxidation with a strongly alkaline permanganate solution, it yields a small quantity of phthalic acid, together with *orthocarboxylic-phenylglyoxylic acid*,  $\text{COOH.C}_6\text{H}_4.\text{CO.COOH}$ . This acid is obtained in nearly the theoretical quantity; it is crystalline, melts at  $138\text{--}140^\circ$ , yields a sublimate of phthalic anhydride on further heating, and is readily soluble in water. The barium salt,  $\text{C}_9\text{H}_4\text{O}_5\text{Ba} + 2\text{H}_2\text{O}$ , crystallises in colourless hexagonal tables, very sparingly soluble in water. The acid appears to be identical with that obtained by Zincke and Breuer (this vol., p. 270), by the oxidation of the oxyquinone prepared from cinnamic alcohol, although the melting point of this latter acid is given as  $177\text{--}197^\circ$ .

*Phthalidcarboxylic acid*,  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} > \text{CH.COOH}$ , is prepared by the action of sodium amalgam on orthocarboxylic-phenylglyoxylic acid; it crystallises in silky plates, melts at  $149.5^\circ$  (uncorr.), and is readily soluble in water and chloroform. When heated at  $180^\circ$ , carbonic anhydride is abundantly evolved and phthalide formed.

A. J. G.

**Amidobenzoic Acid Derivatives of Succinic, Sebacic, and Phthalic Acids.** By G. PELLIZZARI (*Ber.*, 18, 214—216).—This is a continuation of Schiff's work on oxalamido-acids (*Abstr.*, 1884, 906). When a solution of metamidobenzoic acid (10 grams) in ethyl succinate (20 c.c.) and alcohol (10 c.c.) is boiled for two days in a reflux apparatus, *succinyldibenzamic acid*,  $\text{C}_2\text{H}_4(\text{CO.NH.C}_6\text{H}_4.\text{COOH})_2$ , and *ethyl benzamsuccinate*,  $\text{COOH.C}_6\text{H}_4.\text{NH.CO.C}_2\text{H}_4.\text{COOEt}$ , are produced; the former, which was described by Muretow (this Journal, 1872, 1097), separates as a white crystalline powder. The more soluble ethyl benzamsuccinate crystallises from hot water in lustrous scales melting at  $174^\circ$ . With ammonia, it yields *benzamsuccinamide*,  $\text{COOH.C}_6\text{H}_4.\text{NH.CO.C}_2\text{H}_4.\text{CONH}_2$ , melting at  $228\text{--}229^\circ$ , and with aniline, *benzamsuccinanilide*,  $\text{COOH.C}_6\text{H}_4.\text{NH.CO.C}_2\text{H}_4.\text{CO.NHPh}$ , melting at  $252^\circ$ . *Benzamsuccinic acid*, obtained by saponifying the ethyl salt with barium hydroxide, forms colourless prisms melting at

222—223°. It loses 1 mol.  $\text{H}_2\text{O}$  when melted, and is converted into *succinylamidobenzoic acid*,  $\text{C}_2\text{H}_4\text{<}\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\text{>N.C}_6\text{H}_4\text{.COOH}$ , melting at 235° (see also Muretow, *loc. cit.*).

When ethyl sebate (30 c.c.) is boiled with amidobenzoic acid (10 grams) and alcohol (10 c.c.), *sebacyldibenzamic acid*,



and *ethyl benzamsebate*,  $\text{COOH.C}_6\text{H}_4\text{.NH.CO.C}_8\text{H}_{16}\text{.COOEt}$ , are produced; the first forms a white powder sparingly soluble in the usual solvents, melts at 275°, and yields readily soluble salts with the alkalis. Ethyl benzamsebate forms lustrous scales melting at 146°, and yields a barium salt crystallising in magnificent silvery plates. Ammonia and aniline react on the ether only at a moderately high temperature, with production of amidobenzoic acid, amidobenzanilide, sebamide, and sebanilide; this last substance forms silvery scales melting at 198°. *Benzamsebacic acid*,  $\text{COOH.C}_6\text{H}_4\text{.NH.CO.C}_8\text{H}_{16}\text{.COOH}$ , forms colourless prisms melting at 192—193°.

Ethyl phthalate reacts with amidobenzoic acid in the absence of alcohol, yielding *phthalamidobenzoic acid*,  $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\text{>N.C}_6\text{H}_4\text{.COOH}$ , melting at 282°, and *ethyl phthalamidobenzoate*, crystallising in colourless, concentrically grouped needles melting at 152°. This ether is also obtained on heating phthalamidobenzoic acid with ethyl phthalate.

A. K. M.

**Compounds of Hydrazines with Ketonic and Aldehydic Acids.** By A. ELBERS (*Annalen*, **227**, 340—357).—*Phenylhydrazinephenylglyoxylic acid* is precipitated when hydrochloric acid solutions of phenylhydrazine and phenylglyoxylic acid are mixed together. The acid is soluble in ether, chloroform, benzene, and also, with partial decomposition, in hot alcohol. It melts at 153° with evolution of carbonic anhydride and formation of benzylidenephénylhydrazine:  $\text{N}_2\text{HPh : CPh.COOH} = \text{N}_2\text{HPh : CHPh} + \text{CO}_2$ . On reduction with sodium amalgam, the acid decomposes into aniline and phenylamidoacetic acid.

*Phenylhydrazidophenylacetic acid*,  $\text{N}_2\text{H}_2\text{Ph.CHPh.COOH}$ , is formed as an intermediate product in this reaction. It resembles phenylhydrazidopropionic acid in its properties (Fischer and Jourdan, *Abstr.*, 1884, 53). The acid melts at 158° with decomposition, forming benzylidenephénylhydrazine.

*Ethylphenylhydrazinephenylglyoxylic acid*,  $\text{N}_2\text{EtPh : CPh.COOH}$ , is formed together with a substance of the composition  $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}$ , when phenylglyoxylic acid is added to a solution of ethylphenylhydrazine in glacial acetic acid. The crude product is dried, extracted with ether, and treated with caustic soda, which dissolves out the ethylphenylhydrazinephenylglyoxylic acid. On recrystallisation from alcohol, the acid is obtained in rhombic plates, melting at 109° with decomposition. It is decomposed by boiling with hydrochloric acid, yielding ethylaniline and benzaldehyde, and on reduction with sodium amalgam, it splits up into ethylaniline and phenylamido-

acetic acid. The compound of the composition  $C_{16}H_{17}N_3O$ , which is insoluble in caustic soda, appears to be an amide of ethylphenylhydrazinephenylglyoxylic acid.

*Methylphenylhydrazinephenylglyoxylic acid* crystallises in plates and is soluble in alcohol, ethyl acetate, benzene, and acetone. It melts at  $116^\circ$  with decomposition, splitting up into carbonic anhydride, benzaldehyde, methylaniline, and benzylidene-methylphenylhydrazine. The latter forms needle-shaped crystals, which soften at  $102^\circ$  and melt at  $104.5^\circ$ .

*Phenylhydrazineglyoxylic acid*,  $N_2HPh : CH.COOH$ , is soluble in alcohol, acetone, and acetic acid; also in water with slight decomposition. The acid decomposes when it is heated to  $137^\circ$ , yielding aniline, ammonia, hydrocyanic acid, and other products. On cautious reduction with sodium amalgam, *phenylhydrazidoacetic acid* is obtained. It is deposited from an alcoholic solution in silvery plates melting at  $157^\circ$  with decomposition.

*Ethylphenylhydrazineglyoxylic acid*,  $N_2EtPh : CH.COOH$ , crystallises in needles melting at  $121^\circ$  with decomposition. The acid is soluble in the usual solvents.

*Phenylhydrazinemesoxalic acid*,  $N_2HPh : C(COOH)_2$ , melts between  $158^\circ$  and  $164^\circ$ . It crystallises easily from its solutions in alcohol, ethyl acetate, acetic acid, benzene, acetone, and hot water.

*Ethylphenylhydrazineglyoxal*,  $N_2EtPh : CH.CH : N_2EtPh$ , is precipitated when the sodium sulphite compound of glyoxal is added to a slightly acid solution of ethylphenylhydrazine. The compound is soluble in benzene, ethyl acetate, chloroform, acetone, and carbon bisulphide. It melts at  $148-149^\circ$  and decomposes at a higher temperature. W. C. W.

**Orthonitranilinesulphonic Acid: New Method of Preparing Orthonitraniline.** By R. NIETZKI and T. BENCKISER (*Ber.*, 18, 294—296). — *Orthonitranilinesulphonic acid*,  $NH_2.C_6H_3(NO_2).SO_3H$  [1:2:4], is obtained by nitrating sodium acetylsulphanilate, and afterwards boiling the product of the reaction with dilute sulphuric acid to complete the removal of the acetyl-group; it is also obtained by treating acetanilide with Nordhausen sulphuric acid, and then nitrating the sulphonic acid formed. The potassium salt,  $NO_2.C_6H_3(NH_2).SO_3K$ , crystallises in lustrous brown plates. By heating it with concentrated hydrochloric acid at  $170-180^\circ$ , the sulphonic group is readily eliminated and orthonitraniline formed. This process is recommended as being the most convenient for the preparation of orthonitraniline. A. J. G.

**New Synthesis of Aromatic Sulphones.** By R. OTTO (*Ber.*, 18, 246—250). — This consists in heating mercury diphenyl with benzenesulphonic chloride and benzene in sealed tubes at  $160^\circ$ ; the liquid becomes dark coloured, mercury-phenyl chloride is produced together with *benzenesulphone*; the yield of this is, however, small, being at most 1 gram from 20 grams of mercury-diphenyl. Benzenesulphonic chloride and mercury-diphenyl do not appear to react to any appreciable extent when heated at the atmospheric pressure. When the



experiment is performed below  $160^{\circ}$ , the liquid does not become so dark, but the reaction is extremely slow. If equal parts of mercury-diphenyl and benzenesulphonic chloride are heated at about  $254^{\circ}$ , without the addition of benzene, a violent reaction occurs, mercury and benzene vapours, also hydrogen chloride and diphenyl are given off, whilst tar-like and frequently black carbonaceous products are produced. Similar results are obtained on heating mercury-diphenyl with 5—6 times its weight of benzenesulphonic chloride in a closed tube; but in this case compounds of mercaptan-like odour and sulphurous anhydride were also produced.

*Phenylparatolylsulphone* may likewise be obtained in small quantity by heating mercury-diphenyl with tolueneparasulphonic chloride and benzene for 15 hours at  $120^{\circ}$ .  
A. K. M.

### Action of Sodium Phenylsulphinate on Methylene Iodide.

By A. MICHAEL and G. M. PALMER (*Amer. Chem. J.*, **6**, 253—257).—An alcoholic solution of phenylsulphonic acid (2 mols.), methylene iodide (1 mol.), and sodium (1 mol.), dissolved in alcohol, were heated for 4—5 hours at  $120^{\circ}$ . The alcohol was removed by evaporation, water added, and the oily product recrystallised from alcohol. *Methylene iodophenylsulphone*,  $\text{SO}_2\text{Ph}\cdot\text{CH}_2\text{I}$ , thus formed, crystallises in rhombic prisms and melts at  $64\cdot5^{\circ}$ . On heating together two equivalents of sodium phenylsulphinate and one of methylene iodide at  $180^{\circ}$ , *methylphenylsulphone*,  $\text{SO}_2\text{MePh}$ , is formed. It may be crystallised from hot water, melts at  $88^{\circ}$ , and is also formed by the action of sodium phenylsulphinate on methylene iodophenylsulphone, or on methyl iodide.

By the action of sodium ethoxide and of sodium phenylate at  $100^{\circ}$  on the above iodosulphone, methylphenylsulphone is also formed. The reduction of the iodo-compound by sodium ethoxide finds a counter reaction in the conversion of iodoform into methylene iodide by the same reagent. The authors see in the difficulty with which the atom of iodine in the iodosulphone is acted on, a reason for supposing that the two atoms of iodine in methylene iodide possess different functions.  
H. B.

**Formation of Sulphones from Alkylsulphonated Acids of the Series  $\text{C}_n\text{H}_{2n}\text{O}_2$ .** By R. OTTO (*Ber.*, **18**, 154—162).—When phenylsulphonethyl alcohol (this vol., p. 262) is oxidised by means of potassium dichromate and sulphuric acid, a compound is obtained having the composition and properties of the phenylsulphonacetic acid,  $\text{PhSO}_2\text{CH}_2\text{COOH}$ , prepared by the action of sodium benzenesulphinate on sodium chloracetate (*Abstr.*, 1881, 716). With the view to prepare the acid by this latter method, the author dissolved equivalent quantities of chloracetic and benzenesulphinic acids in water, neutralised with potassium hydroxide (Gabriel employed sodium hydroxide, *loc. cit.*), evaporated the solution until the potassium chloride separated, and finally heated the mass as long as aqueous vapour was given off. On treating the product with water, a brown oil remained undissolved; this soon crystallised and was found to be *methylphenylsulphone*,  $\text{PhSO}_2\text{Me}$  (m. p.  $88-89^{\circ}$ ), whilst the aqueous solution con-

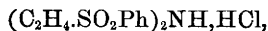
tained a considerable quantity of potassium carbonate and only a little of the phenylsulphonacetic acid sought for. This led to the assumption that potassium phenylsulphonacetate is first formed, but subsequently decomposed according to the equation:  $2\text{PhSO}_2\text{CH}_2\text{COOK} + \text{H}_2\text{O} = 2\text{PhSO}_2\text{Me} + \text{K}_2\text{CO}_3 + \text{CO}_2$ . Barium phenylsulphonacetate suffers a similar decomposition at about  $110^\circ$ ; the sodium salt, at  $120^\circ$ , whilst the potassium salt is partially decomposed even at  $100^\circ$ . The decomposition is more readily effected by the action of an excess of alkali on the acid, and may also be brought about by heating the latter at  $160$ – $200^\circ$ . *Methylparatolylsulphone*,  $\text{C}_7\text{H}_7\text{SO}_2\text{Me}$ , melting at  $86$ – $87^\circ$ , may in the same way be obtained by the action of concentrated potassium hydroxide on *paratolylsulphonacetic acid*; this latter, prepared from sodium paratoluenesulphinic acid and ethyl chloracetate, crystallises in thick vitreous plates melting at  $117$ – $119^\circ$ ; the amide forms small lustrous needles and scales melting at  $163$ – $164^\circ$ . Ethylphenylsulphone, melting at  $41$ – $42^\circ$ , and ethylparatolylsulphone, melting at  $55$ – $56^\circ$ , are also produced when  $\alpha$ -phenylsulphonepropionic acid,  $\text{CH}_3\text{CH}(\text{SO}_2\text{Ph})\text{COOH}$ , and paratolylsulphonepropionic acid,  $\text{CH}_3\text{CH}(\text{SO}_2\text{C}_6\text{H}_4)\text{COOH}$ , are acted on by concentrated potash. The ethyl salts of phenylsulphonepropionic and paratolylsulphonepropionic acids are prepared by heating sodium, benzene, and paratoluenesulphinates with ethyl chloropropionate. On mixing alcoholic solutions of ethyl chlorocarbonate and sodium benzenesulphinic acid (with the view of obtaining phenylsulphoneformic acid), carbonic anhydride is abundantly evolved, the solution becomes acid from the presence of free sulphonic acid, and a neutral liquid substance is produced which is insoluble in water and yields ethyl alcohol and potassium benzenesulphinate when heated with potash. The experiments are being continued. A. K. M.

**Disulphones.** By R. OTTO and H. DAMKÖHLER (*J. pr. Chem.* [2], **30**, 321–366).—A polymeride of the ether of phenylethylsulphone,  $\text{O}(\text{C}_2\text{H}_4\text{SO}_2\text{Ph})_2$ , is formed by the action of potash on ethylenediphenylsulphone. It crystallises in monoclinic plates melting at  $88^\circ$ , and is soluble in water and in alcohol.

Aqueous ammonia converts ethylene diphenylsulphone into ammonium benzenesulphinate and a substance of the formula



The base is deposited from benzene in needles and from alcohol in triclinic plates which melt at  $77^\circ$ . The *hydrochloride*,



forms silky needles soluble in hot alcohol and in hot water, and melts at  $192^\circ$ . The *platinochloride* crystallises in plates which dissolve more freely in alcohol than in water. The *aurochloride* forms yellow silky needles. The *nitrate* is less soluble than the hydrochloride; it melts at  $189^\circ$  with decomposition. The base can also be obtained by the action of ammonia on phenylsulphonethyl chloride or phenylsulphonethyl alcohol. On heating a mixture of methyl iodide, alcohol, and

the base, in sealed tubes at  $115^{\circ}$ , *diphenylsulphone-ethylmonomethylamine* is produced.

Ethylamine converts ethylenediphenylsulphone into a base of the formula  $\text{PhSO}_2\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2\text{Et}$ , and ethylamine benzenesulphinate. The hydrochloride of this base forms a hygroscopic crystalline mass, which is soluble in water and also in absolute alcohol.

Phenylsulphonethyl alcohol is oxidised to phenylsulphoneacetic acid by potassium dichromate and sulphuric acid. Nascent hydrogen decomposes the acid, forming acetic and benzenesulphinic acids.

When a warm alcoholic solution of potassium sulphhydrate acts on phenylsulphone-ethyl chloride, hydrogen sulphide is evolved, and *diphenylsulphonethyl sulphide*,  $(\text{C}_2\text{H}_4\cdot\text{SO}_2\text{Ph})_2\text{S}$ , is formed. The compound crystallises in silky needles, melts at  $123^{\circ}$ , and dissolves in warm alcohol.

Ethylenediphenylsulphone is decomposed by boiling with an alcoholic solution of potassium cyanide, yielding ammonia, benzenesulphinic and succinic acids, and probably ethylene cyanide as an intermediate product. On oxidation with potassium permanganate, the sulphone splits up into oxalic, carbonic, sulphuric, and benzenesulphonic acids. Mono- and di-sulphonic acids are produced by the action of sulphuryl chloride on ethylenediphenylsulphone.

*Ethylenediparatolylsulphone* resembles ethylenediphenylsulphone in its properties, mode of preparation, and in its derivatives. It melts at  $200^{\circ}$ , and is somewhat less soluble than the diphenyl compound. When reduced with sodium-amalgam, it yields ethyl alcohol and paratolylsulphinic acid, melting at  $84^{\circ}$ .

*Paratolylsulphonethyl alcohol*,  $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$ , forms white needle-shaped crystals, melts at  $54^{\circ}$ , and is soluble in ether, benzene, and in hot alcohol. It can be prepared by the action of glycol chlorhydrin on sodium paratoluenesulphinate. The *chloride* crystallises in needles or plates melting at  $78^{\circ}$ , which are soluble in warm alcohol. The *iodide* melts at  $100^{\circ}$ , and dissolves in warm alcohol or benzene. The *benzoate* melts at  $175^{\circ}$ , is soluble in hot benzene. *Diparatolylsulphonethyl sulphide*,  $(\text{C}_2\text{H}_4\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7)_2\text{S}$ , is insoluble in water. It melts between  $150^{\circ}$  and  $160^{\circ}$ . *Diparatolylsulphonethyl oxide*,  $(\text{C}_2\text{H}_4\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7)_2\text{O}$ , forms needle-shaped crystals melting at  $83^{\circ}$ , and is soluble in alcohol, ether, chloroform, and benzene. *Diparatolylsulphonethylamine*,  $\text{NH}(\text{C}_2\text{H}_4\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7)_2$ , is a thick liquid, which unites with acids, forming crystalline salts. The decomposition of this sulphone by potassium cyanide is analogous to the decomposition which ethylenediphenylsulphone undergoes under similar treatment.

The authors also point out that the substance they described (Abstr., 1880, 811) as "ethylenediparatolylsulphone," probably consisted of ethylenediparatolylsulphone. W. C. W.

**Orthiodotoluenesulphonic Acid.** By C. MABERY and G. H. PALMER (*Amer. Chem. J.*, **6**, 170—171).—Orthiodotoluene treated carefully with sulphuric anhydride, yields the above acid, of which the following salts have been prepared:—

*Barium orthiodotoluenesulphonate*,  $\text{Ba}(\text{C}_7\text{H}_6\text{ISO}_3)_2 + 1\frac{1}{2}\text{H}_2\text{O}$ , crystallises in clusters of needles soluble in water.

*Calcium orthiodotoluenesulphonate*,  $\text{Ca}(\text{C}_7\text{H}_6\text{ISO}_3)_2 + 2\frac{1}{2}\text{H}_2\text{O}$ , and *lead orthiodotoluenesulphonate*,  $\text{Pb}(\text{C}_7\text{H}_6\text{ISO}_3)_2 + 2\text{H}_2\text{O}$ .

The acid prepared from the barium salt was obtained as an oily liquid, which does not solidify at  $0^\circ$ . P. P. B.

**Phenylcoumarinsulphonic Acids.** By T. CURATOLO (*Gazzetta*, **14**, 257—264).—The phenylcoumarin prepared by Ogialoro's process (*Abstr.*, 1880, 164) yields a mono- or a di-sulphonic acid according to the conditions of the reaction. The *mono*-acid,  $\text{C}_{15}\text{H}_9\text{O}_2\cdot\text{SO}_3\text{H}\cdot 2\frac{1}{2}\text{H}_2\text{O}$ , obtained by the action of sulphuric with pyrosulphuric acid on phenylcoumarin at the ordinary temperature, crystallises in small white needles, melting with incipient decomposition at  $262^\circ$ . It is sparingly soluble in cold, but readily soluble in hot water. Only 1 mol.  $\text{H}_2\text{O}$  can be removed by desiccation or heating. The *barium* salt crystallises in brilliant scales, moderately soluble in water, the *lead* salt in white needles, resembling, as regards its solubility, the chloride. The *disulphonic* acid,  $\text{C}_{15}\text{H}_8\text{O}_2(\text{SO}_3\text{H})_2\cdot 6\text{H}_2\text{O}$ , obtained by the action of pyrosulphuric acid on the coumarin, is a very deliquescent substance, melting at  $88^\circ$ ; by long desiccation it loses a part of its water. Its *barium* salt crystallises in white prisms very soluble in water, the *lead* salt in acicular prisms. The acids described above are analogous to the coumarin-mono- and di-sulphonic acids described by Perkin.

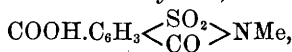
V. H. V.

#### New Class of Compounds Analogous to the Phthaleïns.

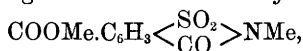
By I. REMSEN (*Amer. Chem. J.*, **6**, 180—181).—By heating potassium orthosulphobenzoate with resorcinol and sulphuric acid, a substance is formed which dissolves in sodium hydroxide to form a fluorescent solution, having a slightly redder tint than that of fluorescein. The imide of orthosulphobenzoic acid and the substitution-products of the acid give rise to a similar series of compounds, which the author considers as analogous to the phthaleïns, and proposes to style sulphon-phthaleïns, regarding them as containing the CO-group of the phthaleïns replaced by  $\text{SO}_2$ . P. P. B.

**Phthalic-sulphinide.** H. N. STOKES (*Amer. Chem. J.*, **6**, 262—283).—Hydrogen potassium anhydro-sulphamine-phthalate was prepared according to Comstock's directions (*Abstr.*, 1884, 319). When treated with alkaline carbonates, the *normal potassium salt*,  $\text{COOK}\cdot\text{C}_6\text{H}_3<\text{SO}_2>\text{NK}$ , is formed. The *mono-silver salt* and the *normal silver salt* are formed by precipitation of the corresponding potassium salts and are very sparingly soluble in water; both contain one molecule of water. An acid lead salt could not be obtained; the *normal lead salt* has the formula  $\text{C}_6\text{H}_3\text{O}_5\text{Pb} + \text{H}_2\text{O}$ . The barium and ammonium potassium salts are also mentioned. By treating the hydrogen, potassium, or silver salts with hydrochloric acid, *anhydro-sulphaminephthalic acid*, or *phthalic-sulphinide*,  $\text{COOH}\cdot\text{C}_6\text{H}_3<\text{SO}_2>\text{NH} + 2\text{H}_2\text{O}$ , is obtained; it is readily soluble in hot water, and crystallises in spherical tufts of slender needles; the melting point is not constant

owing to decomposition. By the action of methyl iodide on the anhydrous mono-silver salt the *monomethyl salt*,

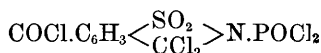


is easily formed, melting at  $191^\circ$ . The *dimethyl salt*,

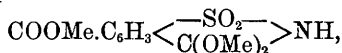


is formed from the preceding by the action of phosphorus pentachloride and methyl alcohol, and also from the normal lead and silver salts; it melts at  $180^\circ$ .

When the anhydrous hydrogen potassium salt is treated with phosphorus pentachloride and the product crystallised from phosphorus oxychloride, a substance of the formula

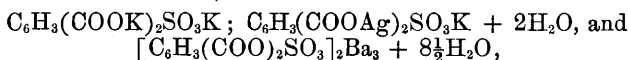


is obtained; this when treated with methyl alcohol yields *trimethyl-anhydrosulphaminephthalate*,



melting at  $144^\circ$ . As the dimethyl salt already described is formed by the action of phosphorus pentachloride followed by that of methyl alcohol, the author concludes that it is the hydrogen of the imido-group that is replaced in the acid salts.

Phthalic-sulphinide is converted into  $\alpha$ -sulphophthalic acid by hydrochloric acid at  $150^\circ$ ; the salts



are described.

When hydrogen potassium anhydrosulphaminephthalate is fused with potash,  $\alpha$ -hydroxyphthalic acid is formed; this has been prepared by other means; its constitution is expressed by the formula  $\text{C}_6\text{H}_3(\text{COOH})_2.\text{OH} = 1:2:3$ . The silver salt has the formula  $\text{C}_6\text{H}_3(\text{COOAg})_2.\text{OH}$ .  
H. B.

**Hydrazines of Cinnamic Acid.** By E. FISCHER and J. TAFEL (*Annalen*, **227**, 303—340).—Indazole,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH} \\ | \\ \text{N}-\end{smallmatrix}\rangle\text{NH}$ , is obtained

from orthohydrazinecinnamic acid, which is best prepared by making sodium orthohydrazinecinnamosulphonate into a paste with strong hydrochloric acid; the mixture is gently warmed until it changes into a brown solution. This is nearly neutralised by the addition of potash, and the acid separated by means of sodium acetate. Indazole boils without decomposition at  $269^\circ$ . It crystallises well from ether. Its salts easily dissociate. When dry hydrogen chloride is passed into the ethereal solution, the chloride is deposited as a red oil, soluble in water and alcohol. On adding ether to the alcoholic solution, the chloride is obtained in crystals. The platinochloride is crystalline. The sulphate is crystalline and soluble in water, but the solution

rapidly dissociates into indazole and sulphuric acid. The picrate forms yellow needles soluble in alcohol. Indazole forms crystalline silver and mercuric compounds.

*Nitrosoindazole* is deposited from a solution in light petroleum in golden needles which melt at  $73^{\circ}$ . It is freely soluble in dilute alcohol, but the solution decomposes. *Monobromindazole*,  $C_6H_4N_2Br$ , is formed by the action of water at  $200^{\circ}$  on monobromindazole-carboxylic acid. It crystallises in colourless needles melting at  $124^{\circ}$ . The crystals dissolve in hot water, ether, and hot soda-lye. On the addition of bromine-water to the aqueous solution, dibromindazole is precipitated.

*Dibromindazole*,  $C_6H_3Br_2N$ , is also formed by the action of

hydrobromic acid on monobromindazolecarboxylic acid, or by adding an excess of bromine to a hydrochloric acid solution of indazole. This compound is freely soluble in alcohol, ether, benzene, glacial acetic acid, ethyl acetate, and warm chloroform. It crystallises in colourless needles melting at  $239^{\circ}$ .

*Ethylindazole*,  $C_6H_4N_2Et$ , prepared by the action of ethyl

iodide on indazole at  $100^{\circ}$  is an oily liquid soluble in water. The *sulphate* and *picrate* crystallise well. They are soluble in alcohol; the former is decomposed by hot water, but the latter may be recrystallised from water.

*Methylindazole*,  $C_6H_4N_2Me$ , is prepared by gradually adding a

solution of sodium nitrite to a mixture of amidoacetophenone hydrochloride and hydrochloric acid. When the crystalline mass dissolves, the liquid is poured into a solution of sodium sulphite; after the mixture has been left at rest for some time, the sodium salt of methylindazolesulphonic acid,  $C_6H_4N_2Me \cdot N \cdot SO_3Na$ , crystallises out. In order to obtain methylindazole from this compound, the acid solution is treated with sodium amalgam, and afterwards boiled with strong hydrochloric acid. The base is liberated by the addition of soda and extracted with ether. Methylindazole melts at  $113^{\circ}$ , and boils at  $280^{\circ}$ . It dissolves freely in alcohol, ether, chloroform, and in hot water. The salts of this base are more stable than those of indazole. The *chloride* is soluble in water and alcohol; but the aqueous solution is decomposed by heat. The *platinochloride* forms needle-shaped crystals. It is decomposed by hot water. The crystalline *sulphate* and *picrate* are sparingly soluble in cold alcohol. Methylindazole forms crystalline compounds with silver nitrate and mercuric chloride.

The *nitrosamine* melts at  $60.5^{\circ}$ . It dissolves freely in alcohol, ether, chloroform, glacial acetic acid, and in warm light petroleum. It also dissolves in hot water, with partial decomposition.

*Ethylmethylindazole*,  $C_6H_4N_2MeEt$ , prepared by the action of

ethyl iodide on methylindazole, is an oily liquid soluble in alcohol and ether. The sulphate and chloride are soluble in water and in alcohol. The *platinochloride* is deposited from hot dilute hydrochloric acid in flat needles.

*Dimethylindazole*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe} \\ | \\ \text{N} \end{array} \text{NMe}$ , forms colourless plates melting

at  $79^\circ$  which dissolve freely in alcohol, ether, light petroleum, and hot water. The *sulphate* crystallises in needles. It is soluble in water and in hot alcohol. The *platinochloride* and *picrate* are crystalline salts.

*Indazolacetic acid*,  $\text{N} \begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{NH} \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{COOH}$ , is rapidly formed when an alkaline solution of orthohydrazinecinnamic acid is exposed to the air, even in presence of reducing agents. It is also produced by the action of warm hydrochloric acid on sodium diazocinnamosulphonate, but the first method gives the best yield. Indazolacetic acid is deposited from its aqueous solution in needles which are soluble in alcohol, glacial acetic acid, acetone, and hot water. It combines with acids and with bases, forming salts.

The *copper salt*,  $(\text{C}_9\text{H}_5\text{O}_2\text{N}_2)_2\text{Cu} + 2\text{H}_2\text{O}$ , is insoluble in water but dissolves in hot alcohol, from which it is deposited in green needles. The lead, silver, and mercury salts are soluble in hot water. The acid melts at  $168-170^\circ$ , and decomposes, forming methylindazole and carbonic anhydride.

*Nitrosoindazolacetic acid* crystallises in golden needles soluble in alcohol, ether, chloroform, ethyl acetate, glacial acetic acid, and in alkalis. If the crystals are deposited from solution in ethyl acetate they melt at  $123^\circ$  with decomposition, but if they are deposited from any other solvent they melt at  $96^\circ$ .

*Monobromindazolacetic acid* dissolves in acetic acid and alcohol, and is sparingly soluble in hot water. The acid melts at  $200^\circ$  with decomposition. On oxidation with chromic acid, it is converted into *monobromindazolcarboxylic acid*,  $\text{N} \begin{array}{c} \text{C}_6\text{H}_4\text{Br} \\ | \\ \text{NH} \end{array} \text{C} \cdot \text{COOH}$ , which is decomposed by heat, or by the action of water at  $200^\circ$ , yielding monobromindazole. The carboxylic acid is deposited from hot acetic acid in yellow needles.

Ethylisindazolacetic acid, formerly termed ethylquinazolecarboxylic acid, is prepared by the reduction of nitrosoethylamidocinnamic acid. The reaction takes place in two stages: ethylhydrazinecinnamic acid is first formed, which oxidises on exposure to the air. A solution of the nitroso-product in glacial acetic acid is treated with zinc-dust, it is then filtered and evaporated in a vacuum, and afterwards diluted with water. It is boiled with sodium carbonate to precipitate the zinc. The filtrate after being well shaken up with air is acidified with hydrochloric acid, which throws down ethylisindazolacetic acid in the form of a crystalline precipitate.

1'. 3' Ethylmethylinindazole, previously described as ethylquinazole, is formed by the action of zinc-dust on a solution of the ethylamido-

acetophenonenitrosamine. 1'.3' Dimethylisindazole melts at 36.5°. Its salts crystallise well but their aqueous solutions easily dissociate. The *chloride* and *sulphate* crystallise in needles, and the *picrate* in rectangular plates. When oxidised, *bromethylisindazolacetic acid* yields an aldehyde,  $C_{10}H_9N_2OBr$ , carbonic anhydride, and water. The aldehyde crystallises in prisms soluble in ether, chloroform, acetic acid, benzene, and in hot alcohol. It is converted into monobrom-ethylisindazolcarboxylic acid,  $C_{10}H_9N_2O_2Br$ , when oxidised. This acid forms needle-shaped crystals melting about 210°. It is soluble in ether, alcohol, and chloroform. On distillation, it splits up into monobrom-ethylisindazole, a crystalline substance soluble in alcohol, ether, and chloroform, but insoluble in acids and alkalis. W. C. W

**Benzylindole.** By O. ANTRICK (*Annalen*, **227**, 360—365).—A good yield of benzylphenylnitrosamine is obtained by cautiously adding sodium nitrite to a solution of 10 grams of benzylaniline in 125 c.c. of alcohol, acidified with 8 grams of strong sulphuric acid. The product is poured into water, and the precipitated nitrosamine recrystallised from alcohol, when it is obtained in yellow needles, melting at 58°, freely soluble in alcohol, ether, chloroform, and light petroleum. It is reduced to benzylphenylhydrazine on treatment with zinc-dust and glacial acetic acid. The crude product acts on pyroracemic acid at the ordinary temperature, forming benzylphenylhydrazinepyroracemic acid. Hydrochloric acid converts this substance into benzylindolecarboxylic acid,  $C_{16}H_{13}NO_2$ , a crystalline compound soluble in ether, hot alcohol, and glacial acetic acid. It melts at 195°, and decomposes into carbonic anhydride and benzylindole. After purification by distillation in a current of steam, benzylindole forms a crystalline mass melting at 44.5°. It is soluble in benzene, light petroleum, chloroform, ether, and alcohol. With picric acid it forms a red crystalline precipitate.

*Benzylpseudoisatin* is formed by the oxidation of benzylindole, or more advantageously by the action of sodium hypochlorite on a slightly alkaline solution of benzylindolecarboxylic acid. It crystallises in red silky needles, melting at 131°, and dissolves freely in ether and alcohol. W. C. W.

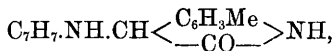
**Formation of Paratolylparamethylimesatin from Dichloroacetic Acid and Paratoluidine.** By C. DUISBERG (*Ber.*, **18**, 190—200).—According to Meyer (*Abstr.*, 1884, 47), the formation of paratolylparamethylimesatin takes place thus:  $-2C_7H_5N + C_2H_2Cl_2O_2 = C_{16}H_{14}N_2O + 2HCl + H_2O + H_2$ . The author finds, however, that the reaction takes place differently; no hydrogen is set free, and an intermediate compound,  $C_{16}H_{16}N_2O$  (*paratolylamidoparamethylloxindole*), is first formed, and then converted by atmospheric oxygen into paratolylparamethylimesatin. In order to obtain paratolylamidoparamethylloxindole, the product of the action of the paratoluidine on dichloroacetic acid is extracted with hot water, and the amorphous residue crystallised from the smallest possible quantity of hot absolute alcohol. After recrystallisation, it is dried over sulphuric acid in an atmosphere of hydrogen. Its formation is expressed thus:—



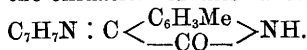
$2C_7H_9N + C_2H_2Cl_2O_2 = C_{16}H_{16}N_2O + 2HCl + H_2O$ . Paratolylamidoparamethyloxindole is readily soluble in hot alcohol, ether, chloroform, carbon bisulphide, and benzene, insoluble or nearly so in light petroleum and water; it crystallises in small white needles, melting at  $166-167^\circ$ . When the colourless alcoholic solution is exposed to the air, it assumes a deep red coloration, and after a time paratolylparamethylmesatin crystallises out. Paratolylamidoparamethyloxindole is insoluble in caustic alkalis and in alkaline carbonates, but yields a blood-red solution with alcoholic potash. With acids it forms salts, the hydrochloride having the composition  $C_{16}H_{16}N_2O.HCl$ . The *diacetyl-derivative*,  $C_{20}H_{20}N_2O_3$ , is readily soluble in benzene, chloroform, carbon bisulphide, and glacial acetic acid, less so in alcohol and ether, and is insoluble in water and in alkalis; it crystallises in white silky needles, melting at  $147^\circ$ , and is not acted on by atmospheric oxygen. The *nitroso-derivative*,  $C_{16}H_{15}N_3O_2$ , forms small bright yellow needles, melting above  $220^\circ$  with decomposition, and dissolves sparingly in water, light petroleum, and benzene, but more readily in alcohol, ether, and chloroform; it gives Liebermann's colour reaction with phenol and sulphuric acid.

When the intermediate product is distilled with zinc-dust, an oil is obtained, which contains, besides paratoluidine, a compound showing the reactions of indole and methylinole.

The author discusses the different ways in which the reaction between dichloroacetic acid and paratoluidine might be expressed, and finds the name (paratolylamidoparamethyloxindole) of the product, on the supposition that it has the constitution



the oxidation of this substance yielding paratolylparamethylmesatin,



*Acetylparatolylparamethylpseudoimesatin*,  $C_{18}H_{16}N_2O_2$ , crystallises in magnificent red lustrous needles; melts at  $121-122^\circ$ , is insoluble in water and alkalis, but readily soluble in the other ordinary solvents. When treated with cold concentrated hydrochloric acid, it yields *acetylparamethylpseudoisatin*,  $C_{11}H_9NO_3$ , identical with the compound obtained on boiling paramethylisatin with acetic anhydride, showing that the acetyl-group in acetylparamethylpseudoimesatin is united with the nitrogen in the nucleus, and that paratolylparamethylmesatin is an imide of paramethylisatin, and not an amide. Acetylparamethylpseudoisatin forms lemon-yellow needles, melting at  $172^\circ$ , is sparingly soluble in water, absolute alcohol, ether, carbon bisulphide, and light petroleum, but more readily in chloroform and benzene. Cold soda and hot sodium carbonate solutions dissolve it readily, with formation of a salt of acetylparamethylisatic acid. This acid may be obtained as a white gelatinous precipitate, and melts at  $172^\circ$  with decomposition; when boiled with glacial acetic acid, it yields acetylparamethylpseudoisatin. *Ethylacetylparamethylisatate*,  $C_{13}H_{15}NO_4$ , crystallises from dilute alcohol in white scales melting at  $78-79^\circ$ . A nitroso-derivative could not be obtained from

paratolylparamethylimesatin. When this is dissolved in absolute alcohol and heated with an excess of sodium ethoxide and ethyl bromide, *ethylparatolylparamethylpseudoimesatin*,  $C_{18}H_{18}N_2O$ , is produced; it forms large orange-red prisms melting at  $151-152^\circ$ , and is decomposed by hydrochloric acid into toluidine and *ethylparamethylpseudoisatin*,  $C_{11}H_{11}NO_2$ . This crystallises from hot water or light petroleum in red needles or prisms melting at  $109-110^\circ$ ; it is not altered by hot concentrated hydrochloric acid, yields the indophenine reaction with concentrated sulphuric acid and coal-tar benzene, the colour being destroyed by alcoholic ammonium sulphide, and on exposure to the air, yellow needles of a reduction-product separate (as in the case of ethylpseudoisatin, Abstr., 1884, 75), and no indigo (as in the case of ethylisatin); the action of glacial acetic acid and zinc-dust also does not produce indigo, showing that the substance is not derived from isatin, but from pseudoisatin. A. K. M.

**Synthesis of  $\alpha$ -Naphthol.** By R. FITTIG and H. ERDMANN (*Annalen*, 227, 242-247).—Jayne (Abstr., 1883, 473) has shown that phenylparaconic acid is decomposed by distillation, forming phenylisocrotonic acid, carbonic anhydride, and a small quantity of phenylbutyrolactone. The authors have observed that  $\alpha$ -naphthol is also one of the products of distillation. When the dry pure acid is quickly distilled, the quantity of naphthol produced is very small, but as much as 25 per cent. (of the weight of the acid) is obtained by slowly distilling imperfectly dried phenylparaconic acid.

$\alpha$ -Naphthol is a condensation-product of phenylisocrotonic acid. A considerable quantity is obtained by boiling the acid for 10 minutes.

W. C. W.

**Nitrosonaphthol and its Derivatives.** By O. HOFFMANN (*Ber.*, 18, 46).—With reference to Ilinski's communication on this subject (this vol., p. 169), the author claims to have prepared the cobalt compounds in 1883, the substances so prepared being patented as dyes by Gans and Co.

L. T. T.

**Azonaphthalene.** By R. NIETZKI and O. GOLL (*Ber.*, 18, 297-299).—Laurent's "naphthase" has of late been generally regarded as azonaphthalene. As, however, both its appearance and properties differ from those to be expected in the latter compound, the authors have endeavoured to prepare azonaphthalenes from other sources. So far they have obtained  $\alpha$ -azonaphthalene, and find it to be entirely different from Laurent's naphthase.

$\alpha$ -Azonaphthalene,  $C_{20}H_{11}N_2$ , is prepared by rubbing amidoazonaphthalene sulphate to a paste with moderately dilute sulphuric acid, and gradually adding somewhat more than the calculated quantity of potassium nitrite; after remaining for about 12 hours at a temperature of  $10-15^\circ$ , the brown flocculent substance formed is collected and boiled with a large quantity of alcohol (of 95 per cent.), when aldehyde and nitrogen are abundantly given off. On adding water to the alcoholic solution, a brown flocculent precipitate is obtained, and is purified by heating with alcohol and animal charcoal, precipitation with water, and repeated crystallisation from

glacial acetic acid.  $\alpha$ -Azonaphthalene so obtained crystallises in slender alizarin-red needles showing blue dichroism, or in larger crystals of dark blue lustre. It melts at  $190^\circ$ , and sublimes even below this temperature in thin yellow plates, which assume a vermilion colour on rubbing. It is insoluble in water, sparingly soluble in alcohol, readily soluble in hot glacial acetic acid and amyl alcohol, very readily soluble in benzene; the solutions are of an intense orange colour. It dissolves in sulphuric acid to a deep blue solution, from which it is precipitated unchanged by water. By the action of acetic acid and zinc, it is reduced to a colourless substance, probably hydrazonaphthalene. The authors are continuing their investigation on the derivatives of this substance, and hope to obtain the isomeric  $\beta$ -azo- and  $\alpha$ - $\beta$ -azo-compounds. The authors confirm the melting point of  $180^\circ$ , assigned by Stultz to amidoazonaphthalene.

A. J. G.

**Derivatives of  $\alpha$ - and  $\beta$ -Naphtholazobenzene.** By L. MARGARY (*Gazzetta*, 14, 271—273).—Typke (*Ber.*, 1877, 1580) was unable to obtain a monobromo-derivative from  $\alpha$ -naphtholazobenzene, whereas the author has already described a corresponding compound from  $\beta$ -naphtholazobenzene,  $C_6H_4Br.N_2.C_{10}H_6.OH$  or  $C_6H_5.N_2.C_{10}H_5Br.OH$  (*Abstr.*, 1883, 326); accordingly he has repeated Typke's experiment, and has been successful in the preparation of two monobromo-compounds, separable by fractional crystallisation from alcohol, and melting at  $185^\circ$  and  $195^\circ$  respectively. Similarly, on brominating  $\beta$ -naphtholazobenzene, the same two monobromo-derivatives are formed. These substances differ in crystalline form, solubility in various menstrua, the coloration of their relative solutions, and in their tinctorial properties. In order to determine the position of the bromine atom, the substance was reduced by tin and hydrochloric acid, when the products formed were 1 : 4 bromaniline and amido- $\alpha$ -naphthol, in accordance with the equation  $C_6H_4Br.N_2.C_{10}H_6.OH + 2H_2 = C_6H_4Br.NH_2 + NH_2.C_{10}H_6.OH$ . Conversely an identical bromo-derivative can be prepared from bromaniline and  $\alpha$ -naphthol through the intervention of the diazo-reaction. A preliminary statement is also made regarding the formation of higher brominated derivatives of  $\beta$ -naphtholazobenzene, which have not yet been isolated, although the crude product of the bromination of this substance yields on reduction a mixture of mono-, di-, and tri-bromaniline.

V. H. V.

**Juglone.** By A. BERNTHSEN and A. SEMPER (*Ber.*, 18, 203—213).—In a paper by Bernthsen (*Abstr.*, 1884, 1368), reasons were given for considering juglone to be a hydroxynaphthaquinone; the phenol-like substance obtained on reducing it must then be a trihydroxynaphthalene  $C_{10}H_5(OH)_3$ . The authors prepare juglone thus: Dry ripe walnut shells are digested with ether for 24 hours at the ordinary temperature, and the extract agitated with dilute chromic mixture (10 parts potassium dichromate, 13 parts sulphuric acid, and 500 parts water), which oxidises any hydrojuglone to juglone; the ether is distilled off, and the residue repeatedly extracted with small quantities of ether to remove fat and resin. The juglone is then dissolved

in chloroform, an equal volume of light petroleum added, the solution filtered and allowed to crystallise. It crystallises in splendid lustrous thin yellowish-red to brownish-red prisms or needles, dissolves very readily in chloroform, readily in hot glacial acetic acid, sparingly in cold alcohol, in ether, and in light petroleum; the melting point is difficult to determine, but appears to be between  $150^{\circ}$  and  $154^{\circ}$ . When sodium ethoxide solution and ether are added to a cold solution of juglone in absolute alcohol, a reddish-brown pulverulent precipitate (sodium-derivative of juglone?) is produced, which yields a purple solution with water. Juglone forms an intense blood-red solution with concentrated sulphuric acid, but is precipitated on dilution; if, however, the solution be heated nearly to boiling, it becomes greenish-brown, and it then yields a dark-green precipitate on dilution. It is decomposed by hot concentrated hydrochloric acid, by a mixture of phosphorus pentachloride and oxychloride, or by the latter alone.

The deviations between the authors' results and those obtained by Mylius (this vol., p. 169) may be explained by the fact that the authors worked with ripe, and Mylius with unripe walnuts.

*Acetyljuglone*,  $C_{10}H_5O_2 \cdot OAc$ , may be prepared by boiling juglone with 4–5 times its weight of acetic anhydride; it dissolves very sparingly in water and in cold alcohol, readily in boiling alcohol and in benzene; moderately in ether, light petroleum, and carbon bisulphide, and is extremely soluble in chloroform; it crystallises in bright yellow pointed plates or in thin flat prisms melting at  $154$ – $155^{\circ}$ .

When juglone (5 grams) is boiled with 20 times its weight of alcohol, and 4.2 grams of pure hydroxylamine hydrochloride with the addition of a few drops of hydrochloric acid, *jugloxime*,  $OH \cdot C_{10}H_5O : NOH$ , is produced; it is precipitated from the cold filtered solution by the addition of water, and crystallised from alcohol. Jugloxime forms magnificent lustrous red needles or thin prisms, melts at  $187$ – $187.5^{\circ}$  with decomposition, and is very readily soluble in hot alcohol and glacial acetic acid, less so in ether, and very sparingly in water; it yields an intense blood-red solution with concentrated sulphuric acid, from which it may be precipitated in orange-coloured flakes; but if the solution has been heated to incipient ebullition, it remains clear on dilution, and assumes a purple colour on the addition of alkali, owing probably to the oxime-group having been eliminated. The separation of the oxime-group is, however, not effected by a mixture of concentrated hydrochloric and glacial acetic acids. Jugloxime does not give Liebermann's reaction with phenol and sulphuric acid. It dissolves in dilute soda solution with blood-red, and in ammonia with yellowish-red coloration. Acetyljuglone also reacts with hydroxylamine hydrochloride, with production of jugloxime. By the action of alcoholic hydroxylamine hydrochloride at  $140^{\circ}$ , jugloxime is apparently converted into the *double oxime*, which crystallises from glacial acetic acid in yellowish needles or thin prisms, and is much more sparingly soluble than jugloxime. It dissolves in alkali with reddish-yellow coloration, and is reprecipitated by acids; it is also soluble in concentrated sulphuric, and to a slight extent in hydrochloric acid. When it is heated to  $215^{\circ}$ , it becomes brown, and detonates a little above  $225^{\circ}$  with carbonisation. Phenylhydrazine also reacts

with juglone. By the action of reducing agents on acetyljuglone a crystalline hydro-derivative (evidently *monacetylhydrojuglone*,



is produced. When juglone is boiled with dilute nitric acid (sp. gr. 1.15), *juglonic acid*,  $\text{C}_8\text{H}_4\text{N}_2\text{O}_6$ , is obtained; it appears to be a *dinitrohydroxyphthalic acid*,  $\text{OH}.\text{C}_6\text{H}(\text{NO}_2)_2(\text{COOH})_2$ . The *ammonium salt*,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_9$ , and the *hydrogen potassium salt*,  $\text{C}_8\text{H}_3\text{KN}_2\text{O}_9$ , are described; they detonate on heating. The acid itself is extremely soluble in water, alcohol, and ether.

*Constitution of Juglone*.—The above experiments show that juglone is a *hydroxynaphthaquinone* which, however, is not identical with the hydroxynaphthaquinone already known; it yields phthalic acid on oxidation. The production of juglonic acid (which is a derivative of hydroxyphthalic acid) indicates that the hydroxyl-group is not in the same benzene nucleus which contains the quinone-groups. In its properties (odour and volatility in steam) juglone bears more resemblance to  $\alpha$ - than to  $\beta$ -naphthaquinone, although like the latter it reacts twice with hydroxylamine. Whether the hydroxyl-group occupies the  $\alpha$ - or the  $\beta$ -position remains to be determined. Mylius' observation that salicylic and metahydroxybenzoic acids are formed when hydrojuglone is fused with potash may be explained on the supposition that the hydroxyl-group occupies the  $\alpha$ -position [ $\text{OH} : \text{O} : \text{O} = 1' : 1 : 4$ ].  
A. K. M.

**Mononitro- $\alpha$ -naphthoic Acids.** By A. E. EKSTRAND (*Ber.*, 18, 73—78).—The author has repeated, with larger quantities of material, his previous experiments (*Abstr.*, 1880, 261) on the action of fuming nitric acid on  $\alpha$ -naphthoic acid in acetic solution. He confirms his previous results, obtaining two mononitro- $\alpha$ -naphthoic acids melting at 215° and 239° respectively, but also obtains a small quantity of a neutral compound.

*Mononitro- $\alpha$ -naphthoic acid* of melting point 215° crystallises in yellowish-white prisms, soluble in boiling alcohol, acetic acid, ether, benzene, and water, much less soluble in these solvents when cold; it does not sublime. The *ethyl salt* crystallises in hard, yellowish octahedra which melt at 68—69°. The sodium, calcium (with  $3\text{H}_2\text{O}$ ), barium, and lead salts are described. This is, without doubt, the acid to which the author formerly ascribed the melting point 194°. A strong ammoniacal solution of this acid was treated with the calculated quantity of ferrous sulphate, the precipitated ferric hydroxide filtered off, the filtrate acidified with acetic acid and allowed to remain for some time. Small violet needles of *amido- $\alpha$ -naphthoid*,  $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_2$ , then formed. This substance is sparingly soluble in ether and water, more easily in alcohol, and melts at 178—179°. It is of a neutral character, and insoluble in solutions of alkaline carbonates. When boiled with caustic alkali, it is dissolved, and acetic acid precipitates from this solution a crystalline substance melting at about the same temperature as the naphthoid. This naphthoid appears to be analogous to the substance melting at 174° which Rakowsky obtained (this Journal, 1873, 391) by the reduction of a mononitro- $\beta$ -naphthoic

acid, and probably has the constitution  $C_{10}H_6 \begin{smallmatrix} \text{CO.NH} \\ \text{NH.CO} \end{smallmatrix} C_{10}H_6$ . The formation of these compounds probably depends on the relative position of the amido- and carboxyl-groups, as the mononitro-acid melting at  $239^\circ$  does not yield such a neutral compound, but an amido-acid. When oxidised with permanganate, the nitro-acid melting at  $215^\circ$  yields hydroxyphthalic acid. When oxidised with nitric acid of sp. gr. 1.3, it yields  $\beta$ -dinitronaphthalene melting at  $169^\circ$  (Beilstein and Kurbatow, *Annalen*, **202**, 224). The nitro- and carboxyl-groups must, therefore, be in the same benzene nucleus. The second *mononitro- $\alpha$ -naphthoic acid* obtained melted at  $239^\circ$ . Graeff (Abstr., 1884, 81) gives  $241$ — $242^\circ$  as the melting point of this acid. 1 part of acid requires 4820 parts of water for solution. The calcium salt crystallises with  $2H_2O$ . By treatment with ferrous sulphate as above, this acid yields an *amido- $\alpha$ -naphthoic acid*. This crystallises from alcohol in needles and melts at  $211$ — $212^\circ$ . It is somewhat soluble in boiling water, but is converted thereby into an isomeric modification melting at  $198$ — $199^\circ$ . When heated above  $212^\circ$  the acid sublimes, forming yellow needles of the isomeric modification. L. T. T.

**Anthracene from Water-gas Tar.** By A. H. ELLIOTT (*Amer. Chem. J.*, **6**, 248—252).—Water-gas tar contains 2.63—2.90 per cent. of anthracene: ordinary coal-tars contain only 0.3—0.4 per cent. The tars examined were obtained by the destructive distillation of light petroleum naphtha boiling below  $150^\circ$ . H. B.

**Retene.** Part II. By E. BAMBERGER (*Ber.*, **18**, 81—85).—In continuation of his previous communication on this subject (Abstr., 1884, 1040), the author describes some further derivatives of retene.

*Retistenequinoxime*,  $C_{14}H_4 \begin{smallmatrix} \text{C:N.OH} \\ | \\ \text{C:N.OH} \end{smallmatrix}$ , obtained from retistenequinone and hydroxylamine, forms glittering golden needles melting at  $128.5$ — $129^\circ$ . It is decomposed into its constituents by hydrochloric acid.

*Retistenequinoxaline*,  $C_{14}H_{14} \begin{smallmatrix} \text{C:N} \\ | \\ \text{C:N} \end{smallmatrix} C_6H_4$ , was obtained by the action

of orthophenylenediamine on the quinone. It crystallises in long silky needles melting at  $164^\circ$ . *Retistenequinol*,  $C_{14}H_{14} : C_2(OH)_2$ , was obtained by heating  $\frac{1}{2}$  gram retistenequinone and 60 c.c. alcohol with a saturated solution of sulphurous acid, in closed tubes at  $60$ — $70^\circ$ . It crystallises in silvery glittering plates, which are rapidly oxidised to the quinone on exposure to the air. If the hydroquinone be suspended in water so that its oxidation by air is very slow, the formation of a brown *retistenequinhidrone* can be observed, which turns green in the presence of alkalis. The quinol can also be obtained by reducing the quinone with zinc and potash. If the quinol is dissolved in boiling potash, and the solution constantly stirred so as to assist oxidation by the air, *potassium-retistenequinhidrone* is precipitated as a voluminous green mass, which is tolerably stable towards oxygen. All the above derivatives closely resemble the analogous derivatives of phenanthrenequinone.

By the action of sodium-amalgam on a boiling alkaline solution of retistenequinone, the author obtained an acid, the silver salt of which gave numbers agreeing with those required for an acid,  $C_{14}H_{14}(COOH)_2$ . This is probably *retistenediphenic acid*, analogous to the phenanthrene-derivative, but the acid itself is so unstable that the author was unable to examine it further. The *copper* and *barium* salts are very sparingly soluble.

From the results of these experiments, the author upholds his formula,  $C_{16}H_{14}O_2$ , for retistenequinone, as against the double formula,  $C_{32}H_{28}O_4$ , or  $C_{32}H_{26}O_4$ , advocated by Ekstrand (Abstr., 1884, 1041).

L. T. T.

**Terpenes and Ethereal Oils.** Part II. By O. WALLACH (*Annalen*, 227, 277—302).—The tetrabromides described in Part I (this vol., p. 171) differ in crystalline form. Hesperidene tetrabromide melting at  $104^\circ$  forms hemihedral crystals belonging to the rhombic system,  $a : b : c = 0.5084 : 1 : 0.4282$ . Citrene bromide melting at  $125^\circ$  is rhombic,  $a : b : c = 0.5238 : 1 : 0.44948$ . It never occurs in hemihedral forms.

To obtain the tetrabromides in a crystalline state, 1 vol. of the terpene is diluted with 4 vols. of alcohol and 4 of ether. The mixture is well cooled with ice, and then 0.7 vol. of bromine is slowly added. The precipitate is washed with cold alcohol and recrystallised from ether.

American oil of turpentine boiling at  $160^\circ$  yields a liquid tetrabromide, but if the oil of turpentine is polymerised by heat, the portion boiling between  $175^\circ$  and  $185^\circ$  yields a solid tetrabromide melting at  $124^\circ$ , which is identical with cynene tetrabromide. A third isomeric tetrabromide is obtained from the highest boiling fraction of the product of the action of equal weights of alcohol and sulphuric acid on oil of turpentine. This tetrabromide crystallises in the monoclinic system. On the other hand, the product of the action of nitric or hydrochloric acid, on oil of turpentine, yields cynene tetrabromide on the addition of bromine.

When the hydrochloride,  $C_{10}H_{16}.2HCl$ , from oil of turpentine is heated with aniline, it is converted into the hydrocarbon  $C_{10}H_{16}$ , which yields cynene tetrabromide. Turpentine monohydrochloride,  $C_{10}H_{16}.HCl$ , does not combine with bromine.

*Pine needle oil* on distillation separates into two fractions. The portion boiling between  $159^\circ$  and  $165^\circ$  yields a liquid tetrabromide, but if the hydrocarbon is heated at  $250^\circ$ , higher boiling products are obtained, which unite with bromine, forming cynene tetrabromide. The fraction of the pine needle oil which boils at  $175$ — $180^\circ$  yields hesperidene tetrabromide. When the ethereal solution of the higher boiling oil is saturated with hydrochloric acid, the di-hydrochloride is obtained. This compound melts at  $49^\circ$ .

Eucalyptus oil does not form a solid bromide, but the liquid boiling at  $180^\circ$ , which is obtained by heating the oil at  $270^\circ$ , yields cynene tetrabromide.

Oil of sage resembles oil of turpentine; it only yields a solid tetrabromide melting at  $124^\circ$  after it has been heated.

Oil of pomegranate (*Ol cort aurant*) consists almost entirely of hesperidene, which boils at  $175^\circ$ , and yields a tetrabromide melting

at 104°. After the hydrocarbon has been heated at 250—270°, it yields, on treatment with bromine, cynene tetrabromide melting at 124°. The hydrochloride of hesperidene,  $C_{10}H_{16}, 2HCl$ , resembles the hydrochloride from oil of turpentine in every respect.

Oil of lemons contains two terpenes, one boiling below 170°, which resembles oil of turpentine; the other boiling between 175° and 180° is identical with hesperidene.

Oil of bergamot contains hesperidene and a terpene boiling between 180° and 190°, which does not form a solid bromide.

Oil of cummel (*Oleum carvi*), oil of dill, and the essential oil from *Erigeron canadense* contain a terpene which is identical with hesperidene.

Caoutchene and isoprene are obtained by the destructive distillation of caoutchouc. Caoutchene is identical with cynene. Isoprene is converted into cynene at a temperature of 250°. Oil of camphor also contains cyuene.

The author proposes to classify the terpenes as follows: A. HEMI-TERPENES or PENTENES,  $C_5H_8$ . B. TRUE TERPENES,  $C_{10}H_{16}$ , divided into the following groups: 1. *Pinenes* (boiling point 160°). 2. *Camphenes* (melting point 50°, boiling point below 160°). 3. *Limonenes* (boiling point 175—177°). 4. *Dipentenenes* (boiling point 181°). C. POLY-TERPENES. 1. *Triptenenes*,  $C_{15}H_{24}$  (boiling point 250—260°), such as cedrene, cubebene, &c. 2. *Tetrapentenenes*,  $C_{20}H_{32}$  (boiling point above 300°), for example, colophene. 3. *Polyterpenes*,  $(C_{10}H_{16})_x$ , such as caoutchouc, &c.

W. C. W.

**Chlorophyll and its Compounds.** By E. GUIGNET (*Compt. rend.*, 100, 434—437).—Chlorophyll which has been isolated by any known method is readily soluble in alcohol, benzene, or light petroleum, but if the fresh or dried leaves are treated directly with light petroleum, the latter dissolves no chlorophyll, but only a mixture of yellow and colourless substances. This fact indicates that the chlorophyll is contained in envelopes which are insoluble in light petroleum but soluble in alcohol, a supposition which is supported by the fact that when dried leaves are powdered and repeatedly exhausted with light petroleum a small quantity of chlorophyll is eventually dissolved, the envelopes being attacked by prolonged treatment with the petroleum. The finer granulations contained in leaves yield a small quantity of chlorophyll to light petroleum, probably because they are not surrounded by resisting envelopes. If the deep green solution obtained by exhausting dried leaves with warm alcohol of 95 per cent. is cooled in a mixture of ice and salt, it deposits a considerable quantity of colourless or yellowish substances, insoluble in light petroleum, and it is probably this complex substance which constitutes the envelopes enclosing the chlorophyll.

Chlorophyll is very unstable in presence of dilute acids or even water, being rapidly converted into a brown flocculent substance, but it is very stable in presence of bases, and behaves like a true acid, as Frémy pointed out a long time ago. The potassium and sodium salts are soluble in water, but insoluble in absolute alcohol and light petroleum; the lead salt is insoluble in water.



To obtain the sodium compound, a decoction of leaves in 95 per cent. alcohol is purified by cooling to  $-10^{\circ}$ , and filtering, then agitated with one-tenth its volume of light petroleum, and mixed with a quantity of water equal to the volume of the original alcohol. The chlorophyll is insoluble in the dilute alcohol, but remains dissolved in the petroleum, whilst the alcohol retains a yellow colouring matter, tannin, salts, &c. The petroleum is then briskly agitated with a solution of sodium hydroxide in 95 per cent. alcohol, and the sodium compound which is formed remains dissolved in the water originally mixed with the alcohol, whilst the petroleum retains yellow and colourless substances. The sodium chlorophyllate is purified by repeated washing with absolute alcohol which removes the excess of alkali. In order to obtain it in crystals, the aqueous solution is mixed with alcohol and evaporated over lime, when the vapour of water is alone absorbed, and the alcohol, becoming more and more concentrated, deposits the sodium chlorophyllate in very dark-green needles, very soluble in water. This compound is not decomposed by water even on heating, and its aqueous solution gives the absorption-spectrum of chlorophyll. When the aqueous solution is mixed with lead acetate, a well-defined deep-green lead chlorophyllate is precipitated, and the calcium, barium, and aluminium salts may be obtained in a similar manner. These compounds seem to be much more definite in character than the chlorophyll lakes previously obtained by Frémy and others.

These results were obtained with leaves of spinach dried at  $50^{\circ}$ , or in a vacuum. The results are the same if fresh leaves are repeatedly treated with a boiling 0.5 per cent. solution of sodium carbonate to remove tannin, pectic substances, &c., and then extracted with 95 per cent. alcohol, or if the dry leaves are first exhausted with light petroleum and then with alcohol. The latter method gives the purest products. Ivy leaves may be used, but they are more difficult to dry and contain a larger proportion of foreign substances.

It would seem that chlorophyll is a much more definite and stable compound than is generally supposed. Unaltered chlorophyll is found in the excretions of many animals, and even in peat.

C. H. B.

**Vincetoxin.** By C. TANRET (*Compt. rend.*, **100**, 277—279).—Coarsely-powdered *Asclepias* root is mixed with milk of lime, extracted with cold water, the solution mixed with sodium chloride, and the precipitate collected, washed with salt solution, dried, and re-dissolved in chloroform. The chloroform solution is decolorised by animal charcoal, the chloroform distilled off, the residue dissolved in its own weight of alcohol, ether added so long as a precipitate forms, and the mixture agitated with half its volume of water. The solution separates into two layers, the lower of which, when evaporated to dryness, yields *vincetoxin soluble in water*. The upper layer is agitated with a dilute alkaline solution to remove a resinous acid, then with dilute sulphuric acid, again neutralised, and the liquid distilled off. The residue, when dried at  $100^{\circ}$ , is *vincetoxin insoluble in water*.

Vincetoxin, soluble or insoluble, is a glucoside of the composition

$C_{16}H_{22}O_6$ , with a laevorotatory power of  $[\alpha]_D = -50^\circ$ . It yields a glucose which does not crystallise, is optically inactive, and does not ferment. Soluble vincetoxin forms an amorphous yellowish powder, very soluble in water, alcohol, and chloroform, but insoluble in ether. It has a sweetish bitter taste, and begins to decompose at  $130^\circ$ . An aqueous solution becomes turbid when heated, but regains its transparency when cooled. Insoluble vincetoxin is also amorphous and very soluble in alcohol, ether, and benzene, but insoluble in water. It dissolves easily, however, in an aqueous solution of soluble vincetoxin. This solution coagulates at a lower temperature than a solution of the soluble variety alone, and by using proper proportions of the two varieties, it is possible to obtain a solution which will gelatinise at  $15^\circ$ . Insoluble vincetoxin melts at  $59^\circ$ .

Although readily soluble in chloroform or water alone, soluble vincetoxin is insoluble in aqueous chloroform. It is precipitated by a number of salts, notably by sodium chloride. With potassium mercuric iodide or with iodine solution, vincetoxin yields precipitates in presence of inorganic acids only, and not in presence of organic acids. The insoluble variety will, however, give a precipitate with these reagents in presence of oxalic acid.

C. H. B.

**Active Constituents of *Skimmia Japonica*.** By J. F. EIJKMAN (*Chem. Centr.*, 1884, 42, 780).—*Skimmia Japonica* is a shrub belonging to the family Rutaceae, growing in Japan. By distillation with steam, the author isolated a brown ethereal dextrorotatory oil of peculiar odour, somewhat resembling that of pomegranate and juniper oils; its sp. gr. = 0.8633 at  $20^\circ$ . The oil scarcely reduces silver solutions, and gives only a slight reaction with sodium hydrogen sulphite. On distillation, the oil yields two principal fractions, the one, an oil boiling at  $170$ – $175^\circ$ , probably a terpene of the formula  $C_{10}H_{16}$ , giving an orange-red coloration with sulphuric acid, a brownish-violet coloration with hydrochloric acid, and thickening, on exposure to air; the other a solid, camphor-like substance,  $C_{10}H_{16}O$ , distilling at  $225$ – $235^\circ$ . The residue in the retort boils above  $250^\circ$ , solidifies in the cold, and is soluble in chloroform.

The alcoholic extract of skimmia wood contains a crystalline glucoside, *skimmin*,  $C_{15}H_{16}O_8 + H_2O$ ; this melts at  $210^\circ$ , does not appear to be poisonous, and has a fine blue fluorescence in alkaline solution. Its aqueous solution is neutral, does not reduce Fehling's solution, or precipitate metallic salts with the exception of basic lead acetate.

When boiled with mineral acids, skimmin is split up into sugar and *skimmetin*,  $C_9H_6O_3$ ; this is a crystalline body, having a fine blue fluorescence, in aqueous, alcoholic, and alkaline solutions, not destroyed on addition of strong sulphuric acid. It gives a blue coloration with ferric chloride, and with gold chloride a red colour changing to violet and ultimately to blue.

H. P. W.

**Morin.** By R. BENEDIKT and C. HAZURA (*Monatsh. Chem.*, 5, 667–677).—The previous study of this compound convinced the authors that the formula of morin is probably  $C_{16}H_{10}O_7$ , a conclusion borne out by the study of its derivatives (*Abstr.*, 1884, 1179).

*Bromo-derivatives of Morin.*—According to Hlasiwetz and Pfaudler (*Sitzungsber. Kais. Akad.*, **50**, 13), morin forms a tribrominated derivative: by treating an alcoholic solution of morin with bromine, the authors have obtained a *monethyl ether of tetrabromomorin*,  $C_{15}H_5Br_4O_7Et + 3H_2O$ , which crystallises from aqueous alcohol in large colourless crystals melting at  $135^\circ$ . *Tetrabromomorin*,  $C_{15}H_6Br_4O_7 + 2\frac{1}{2}H_2O$ , is obtained by treating this compound with hydrochloric acid, or, better still, with stannous chloride and hydrochloric acid. By precipitation with water from its alcohol solutions, it is obtained in fine needle-shaped crystals melting at  $258^\circ$ .

*Morinsulphonic acid*,  $C_{15}H_9O_7.SO_3H$ , is obtained by heating morin with concentrated sulphuric acid. It is sparingly soluble in cold, easily in hot water, is soluble in alcohol and glacial acetic acid, but insoluble in ether. Its aqueous solutions are yellow, the colour being intensified by the addition of an alkali; it dyes wool and silk directly. The *potassium salt*,  $C_{15}H_8KO_7.SO_3K + \frac{1}{2}H_2O$ , crystallises in yellow needles, dissolving in water to form a greenish fluorescent solution. The *barium salt*,  $C_{15}H_8SO_{10}Ba$ , obtained by treating a solution of the acid with barium carbonate, is but sparingly soluble in water; from hot aqueous solutions, it separates on cooling as a yellow flocculent precipitate.

Morinsulphonic acid, treated with bromine, yields *tribromophloroglucinol*, and its barium salt on nitration yields *trinitrophloroglucinol*, which is easily soluble in water and alcohol, and crystallises in microscopic hexagonal crystals melting at  $159$ – $160^\circ$ . Its aqueous solutions yield with baryta a precipitate of the salt  $[C_6(NO_2)_3O_3]_2Ba_3$ .

P. P. B.

**Action of Ethylic Diacetosuccinate on Ammonia and Primary Amines.** By L. KNORR (*Ber.*, **18**, 299–311).—The author has shown that ethylic acetoacetate reacts with primary and secondary amines to form quinoline-derivatives (*Abstr.*, 1884, 302 and 1198; this vol., p. 273), and that ethylic diacetosuccinate reacts with phenylhydrazine to form dimethyloxyquinizine (*Abstr.*, 1884, 302, 1153, and 1377), and expected that the reaction of the ethylic diacetosuccinate with ammonia and primary amines would lead to the formation of similar compounds; his experiments, however, show that substituted

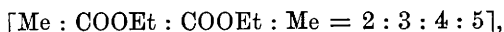
pyrrolidine-derivatives of the general formula

$$\begin{array}{c} \text{COOEt.C:CMe} \\ | \\ \text{COOEt.C:CMe} \end{array} \text{NR}'$$

are formed. These substances are all insoluble in water, acids, and alkalis, readily soluble in alcohol, ether, and chloroform; on hydrolysis, they yield the corresponding acids, and these, when heated at  $200$ – $300^\circ$ , are converted, with loss of carbonic anhydride, into the corresponding substituted pyrrolidines. The acids are all insoluble in water, sparingly soluble in ether, soluble in hot alcohol and glacial acetic acid. The potassium salts are insoluble in alcohol.

*Ethylic dimethylpyrrolinedicarboxylate*,  $C_4NHMe_2(COOEt)_2$ , is obtained by dissolving ethylic diacetosuccinate in concentrated ammonia; it separates after a short time as a yellow oil which soon solidifies to a crystalline mass. Addition of strong acetic acid accelerates the

reaction. It crystallises in fine needles and melts at 90—91°. From its formation, it must have the symmetrical formula—



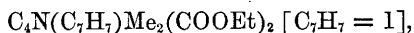
whilst the isomeric compound obtained from ethylic amidoacetate ( $\beta$ -imidobutyrate) (Abstr., 1884, 1368) must have the unsymmetrical constitution  $[\text{COOEt} : \text{Me} : \text{COOEt} : \text{Me} = 2 : 3 : 4 : 5]$ . *Dimethylpyrollinedicarboxylic acid* could not be obtained free from the mon-ethyl salt.

*Ethylic trimethylpyrollinedicarboxylate*,  $\text{C}_4\text{NMe}_3(\text{COOEt})_2$ , prepared from methylamine and ethylic diacetosuccinate, crystallises in thick prisms and melts at 72°. The *free acid*,  $\text{C}_4\text{NMe}_3(\text{COOH})_2$ , forms a fine crystalline precipitate; it turns red on drying, and at 240—245° decomposes with evolution of carbonic anhydride.

*Ethylic phenyldimethylpyrollinedicarboxylate*,

$\text{C}_4\text{NPhMe}_2(\text{COOEt})_2$   $[\text{Ph} : \text{Me} : \text{COOEt} : \text{COOEt} : \text{Me} = 1 : 2 : 3 : 4 : 5]$ , prepared in a similar manner by means of aniline, forms a solid crystalline mass, melts at 37—38°, and distils at 280° under 50 mm. pressure. The *free acid* forms a white powder, and decomposes at 224° into carbonic anhydride and the corresponding pyrroline.

*Ethylic paratolyldimethylpyrollinedicarboxylate*,



crystallises in broad tables, and melts at 67°. The *free acid* crystallises in needles and decomposes at 250°.

*Ethylic  $\beta$ -naphthyldimethylpyrollinedicarboxylate*,



crystallises in needles and melts at 124°. The *free acid* is sparingly soluble in most solvents and decomposes at 260°.

*Ethylic phenyldimethylpyridazindicarboxylate*,  $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_4$ , is obtained by the action of phenylhydrazine on ethylic diacetosuccinate in acetic acid solution. It stands in close relationship to the substances above described. It crystallises in prisms and melts at 127°. The *free acid* crystallises in needles and decomposes at 220° into carbonic anhydride and a crystalline substance not yet investigated.

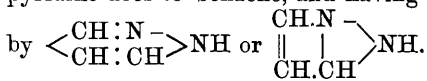
As already mentioned, the pyrollinedicarboxylic acids are decomposed when heated into carbonic anhydride and substituted pyrrolines. These substances form very volatile colourless oils, which soon assume a yellow or red colour on exposure to air, and are resinified by strong acids. Those containing aromatic groups can be crystallised. *Paratolyldimethylpyrroline*,  $\text{C}_4\text{NH}_2\text{Me}_2\text{C}_7\text{H}_7$   $[\text{C}_7\text{H}_7 : \text{Me} : \text{Me} = 1 : 2 : 5]$ , described as an example of the rest, is crystalline, melts at 45—46°, and boils without decomposition at 255° under a pressure of 774 mm. It is readily volatile with steam, and has a peculiar smell like that of rosin. It is insoluble in water, alkalis, and acids, readily soluble in most other solvents.

A. J. G.

### Action of Ethylic Benzoylacetoacetate on Phenylhydrazine.

By L. KNORR and A. BLANK (*Ber.*, 18, 311—317).—This reaction leads

to the formation of a substance which must be regarded as derived from a base,  $C_3N_2H_4$ , standing to pyrroline in the same relation that pyridine does to benzene, and having a constitution expressed either



*Ethyllic methyl-diphenylpyrazenecarboxylate*,  $C_3N_2MePh_2.COOEt$ , is prepared by gradually adding phenylhydrazine (46 parts) to ethyllic benzoylacetoacetate (100 parts); the mass becomes strongly heated, water separates, and after a while the new compound separates, and is purified by washing with ether and recrystallisation from alcohol. It melts at  $121-122^\circ$ , can be distilled unaltered, is readily soluble in chloroform, hot alcohol, ether, light petroleum, and strong acids, but is insoluble in water and alkalis. The *free acid*,  $C_{17}H_{11}N_2O_3$ , is obtained from the ethyl salt by saponification with alcoholic potash, &c. It is crystalline, melts at  $205^\circ$ , is readily soluble in alkalis, ether, chloroform, benzene, and concentrated acids, insoluble in water and dilute acids. It is monobasic; numerous salts were prepared of which the potassium salt,  $C_{17}H_{13}N_2O_2K$ , and silver salt,  $C_{17}H_{13}N_2O_2Ag$ , were analysed.

*Methyl-diphenylpyrazene*,  $C_3N_2HMePh_2$ , is obtained from the acid above described by heating for some time at  $240-260^\circ$ . It is crystalline, melts at  $63^\circ$ , boils at  $355^\circ$  under 750 mm. pressure, is insoluble in water, but soluble in the other usual solvents. It acts as a weak tertiary base; the hydrochloride and nitrate crystallise in needles; the platinumchloride,  $(C_{16}H_{13}N_2)_2H_2PtCl_6 + H_2O$ , forms orange-red needles, and melts with decomposition at between  $160-200^\circ$ . The *methiodide*,  $C_{17}H_{17}N_2I$ , crystallises in needles, melts at  $187^\circ$ , is sparingly soluble in water, soluble in alcohol and chloroform, insoluble in alkalis, ether, benzene, &c. It is resolved into its components on heating. Moist silver oxide converts it into the corresponding ammonium base. The platinumchloride crystallises in orange-red needles and melts at  $241^\circ$ . *Methyl-diphenylbromopyrazene*,  $C_3N_2BrMePh_2$ , obtained by adding bromine to a solution of methyl-diphenylpyrazene, melts at  $75^\circ$ , is soluble in alcohol, ether, and chloroform, insoluble in water and dilute acids; the bromine is not removed by boiling with alcoholic potash. Methyl-diphenylpyrazene is not attacked by acid reducing agents, and only slowly by sodium-amalgam; it is, however, readily reduced by the gradual addition of metallic sodium to its boiling alcoholic solution. *Dihydro-methyl-diphenylpyrazene*,  $C_{16}H_{16}N_2$ , so produced, crystallises in long prisms, melts at  $109^\circ$ , is soluble in concentrated acids, ether, alcohol, benzene, &c., insoluble in water, dilute acids, and alkalis. When treated with nitrous acid in acid solution, the dihydro-base gives an intense coloration, the colour being discharged by alkalis. When heated with hydrochloric acid at  $150^\circ$ , the base is converted into a bluish-green resin.

A. J. G.

**Compounds from Animal Tar.** By H. WEIDEL and B. PICK (*Monatsh. Chem.*, 5, 656-666).—A mixture of bases was obtained from the fraction of animal tar boiling at  $170-180^\circ$ , after oxidation with dilute sulphuric acid and potassium dichromate and removal of

the quinone and fatty acids formed by distillation with steam. These bases were converted into their hydrochlorides by evaporation with hydrochloric acid, and next heated with concentrated sulphuric acid at 190—200° to remove pyrroline, &c. The bases obtained from the sulphates formed a liquid boiling at 162—184°, the chief fraction distilling at 170—180°. This fraction was converted into the platinochlorides, which, by fractional crystallisation, were separated into three portions: (A.) A sparingly soluble crystalline platinochloride, from which lutidine was obtained. (B.) A more soluble but crystalline salt, consisting of the salts of two bases. (C.) A soluble, oily uncrystallisable salt. From this last fraction, a base having the composition  $C_8H_{11}N$ , was obtained. It is a colourless oil, strongly refractive, slightly soluble in water, and boils at 177·8° (bar. 758·4 mm.), its sp. gr. is 0·9286 at 16·8°. On oxidation, it yields *lutidinic acid* melting at 219° (Weidel and Herzig, *Monatsh. Chem.*, **1**, 20). This base is an isomeride of the different known collidines, and from its behaviour on oxidation the authors style it *α-methylethylpyridine*. The results of this investigation also prove Anderson's collidine, b. p. 179°, to be a mixture of several bases. P. P. B.

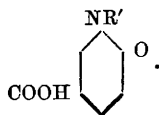
**Commercial Picoline.** By A. LADENBURG and C. F. ROTH *Ber.*, **18**, 47—54).—The authors examined commercial picoline with the object of separating its two constituents, *α*- and *β*-methylpyridine (Weidel, *Abstr.*, 1880, 269), and converting them into the corresponding piperidine bases. The picoline employed was obtained from Kahlbaum and boiled at 125—145°. On distilling, two principal fractions were obtained: I boiling at 132—135°, and II at 139—142°. Both fractions were reduced by treating their alcoholic solutions with sodium.

Fraction I, when thus treated, yielded *α-methylpiperidine*. This was isolated from the products of the reduction by slowly adding carbon bisulphide to the free base. *α-Methylpiperidine α-methylpiperylthiocarbamate*,  $C_8H_{12}N.CS.SH.NH.C_6H_5Me$ , thus prepared, crystallises in colourless needles which melt at 118°, but sublime without change at 100°. It is exceedingly soluble in the usual solvents, and is best crystallised from dry ether. It is decomposed by hydrochloric acid, sulphur being precipitated and *α-methylpiperidine hydrochloride* formed, which crystallises in easily soluble colourless needles, melting at 189°. The free base is a colourless liquid boiling at 118—119°. The *platinochloride* is easily soluble, the *mercuriochloride* sparingly so, the *hydrobromide* yields colourless needles melting at 182°. When treated with iodine dissolved in potassium iodide, the hydrochloride yields a *periodide*. This fraction, and even the higher fractions, also contain pyridine.

Fraction II, when reduced, yielded a mixture of piperidine bases which could not be separated. The unreduced liquid (b. p. 139—142°) was therefore examined. It was found to contain a little *β*-methylpyridine—detected by its yielding pyridinecarboxylic (nicotinic) acid on oxidation—but consisted principally of a *dimethylpyridine* or *lutidine*, which the authors consider to be the *αα'*-compound. This substance was purified by the help of its mercuriochloride,

( $C_7H_9N$ ) $HHgCl_3$ , which crystallises in highly refracting colourless scales, melting at  $186^\circ$ . The free base is a colourless oil which boils at  $142$ — $143^\circ$ , and has a penetrating odour resembling that of oil of peppermint. It is freely soluble in cold, less so in hot water. When oxidised with potassium permanganate, it yields a *pyridinedicarboxylic acid*,  $C_5NH_3(COOH)_2$ , which crystallises in colourless highly refracting prisms or scales melting at  $225^\circ$ , and appears to be the same as that described by Dewar (this Journal, 1871, 144). When reduced in alcoholic solution with sodium, this lutidine yields a piperidine base,  $C_7H_{15}N$ , which boils at  $127$ — $130^\circ$ , and has the disagreeable odour peculiar to these bases. It is a colourless mobile liquid, miscible with water, ether, and alcohol, and has a sp. gr. =  $0.8492$  at  $\frac{4^\circ}{4^\circ}$ . Its *platinochloride* forms large orange crystals melting at  $212^\circ$ , its hydrobromide easily soluble needles. L. T. T.

**Constitution of Pyridine-derivatives derived from Coumalinic Acid.** By H. v. PECHMANN (*Ber.*, 18, 317—319).—Some doubt being felt as to the accuracy of the constitution assigned by the author and Welsh (*Trans.*, 1885, 154) to the acid (methoxynicotinic acid), formed by the methylation of hydroxynicotinic acid or the action of methylamine on coumalinic acid, the subject was reinvestigated. When the acid is treated with sodium-amalgam and water, methylamine is evolved; phenoxynicotinic acid, on similar treatment, yields aniline. These results point to a direct union of the methyl- or phenyl-group with nitrogen instead of to oxygen, and lead to the constitution of the acids being expressed by the general formula



Whether an intermolecular change occurs in their formation, from hydroxynicotinic acid, or whether the latter has a similar constitution, must be settled by further investigation. A. J. G.

**Trimethylquinoline.** By L. BEREND (*Ber.*, 18, 376—377).—1 : 3 : 4 *Trimethylquinoline*,  $C_9H_4Me_3N$ , is prepared by Skraup's reaction from pseudocumidine [ $Me : Me : Me : NH_2 = 1 : 3 : 4 : 6$ ]. It crystallises in lustrous white prisms, melts at  $42$ — $43^\circ$ , and boils at  $285$ — $287^\circ$  (uncorr.). The *nitrate*,  $C_{12}H_{13}N.HNO_3$ , crystallises in asbestos-like needles; the *platinochloride*,  $(C_{12}H_{13}N)_2.H_2PtCl_6 + 2H_2O$ , in sparingly soluble orange-red needles; the *hydrogen sulphate*,  $C_{12}H_{13}N.H_2SO_4$ , forms lustrous white prisms. A. J. G.

**Quinoline-ammonium Bases.** By A. BERNTHSEN and W. HESS (*Ber.*, 18, 29—38).—*Methylquinaldinium hydroxide*,  $C_{10}H_9NMe.OH$ , was obtained by treating a cold aqueous solution of quinaldine methiodide (Doebner and v. Miller, *Abstr.*, 1884, 184) with cold alkali, and extracting with ether. It forms a yellowish resinous mass which undergoes partial decomposition when exposed to the air, apparently forming an





temperature than that necessary to split up an alkylammonium hydroxide into a tertiary amine and an alcohol. L. T. T.

**Diphenylpseudoamphiphenacylnitrile.** By R. MÖHLAU (*Ber.*, 18, 163—168).—Diphenyldiisindole was, at the time of its discovery (*Abstr.*, 1883, 342), considered to be the first representative of the *paranitrides*, but it has since been shown that Staedel's isindole belongs to this class of compounds. The name *amphiphenacylnitrile* is proposed for isindole, and the author points out that it may be represented by

either of the formulæ  $\text{NH} \begin{array}{c} \text{CPh} \cdot \text{CH} \\ | \quad | \\ \text{CH} \cdot \text{CPh} \end{array} \text{NH}$ , or  $\text{N} \begin{array}{c} \text{CPh} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CPh} \end{array} \text{N}$ , but

that its properties appear to be in favour of the second. If this view is correct, diphenyldiisindole cannot be regarded as a phenyl-substitution-derivative of amphiphenacylnitrile, but as derived from the (hypothetical) isomeride. It is therefore named *diphenylpseudoamphiphenacylnitrile*.

When phenacylanilide is distilled, water first comes over with some unaltered substance, and afterwards diphenylpseudoamphiphenacylnitrile, which is obtained pure by re-distillation. It is also produced on heating phenacylanilide hydrochloride with phosphorus pentachloride at  $100^\circ$ :  $-2\text{CPh} \cdot \text{CH}_2 \cdot \text{NHPh} + 2\text{PCl}_5 = \text{C}_{23}\text{H}_{22}\text{N}_2 + 2\text{POCl}_3 + 4\text{HCl}$ .

The supposed *nitroso-derivative*,  $\text{C}_{28}\text{H}_{20}\text{N}_4\text{O}_2$ , previously described (*loc. cit.*), does not behave like nitrosodimethylaniline with phenol and sulphuric acid; it possesses both basic and acid properties, the sodium salt having the composition  $\text{C}_{28}\text{H}_{18}\text{N}_4(\text{ONa})_2$ . It is therefore concluded that this compound is not a true nitroso-derivative, but probably contains the isonitroso-group ( $\text{:NOH}$ ). When the nitrate (*loc. cit.*) is warmed with nitric acid of sp. gr. 1.18, a mixture of mono- and di-nitrodiphenylisonitrosopseudoamphiphenacylnitrile appears to be formed. A. K. M.

**Diquinolines.** By E. OESTERMAYER (*Ber.*, 18, 333—334).—The author confirms Roser's opinion (*Abstr.*, 1884, 1371, and this vol., p. 275) as to the non-identity of diquinoline from benzidine with Weidel's  $\alpha$ -diquinoline, inasmuch as this latter base unites with only one molecule of methyl sulphate to form a compound of the formula  $\text{C}_{18}\text{H}_{12}\text{N}_2 \cdot \text{MeSO}_4\text{H}$ ; this dissolves in alkalis with citron-yellow colour, the aqueous solution not showing the slightest trace of fluorescence. It is thus distinguished sharply from the diquinoline from benzidine which, as already shown by Oestermayer and Henrichsen (this vol., p. 173) gives a strongly fluorescent aqueous solution, and strikes a blood-red coloration with alkalis. A. J. G.

**Quinolinecarboxylic Acid (Cinchonic Acid).** By A. CLAUS and T. MUCHALL (*Ber.*, 18, 362—366).—The oxidation of cinchonine to cinchonic acid is more conveniently effected by nitric acid (sp. gr. 1.3) than by chromic mixture; nitrodioxyquinoline is formed to some extent at the same time. Phosphoric chloride acts on cinchonic acid, forming a substance subliming in yellow needles, apparently cinchonic

chloride hydrochloride,  $C_9NH_5.COCl.HCl$ , it could not, however, be obtained in a pure state. Cinchonic acid unites readily with benzyl or methyl bromide when heated in sealed tubes at  $130-170^\circ$ . The compound with *benzyl bromide*,  $C_{10}H_7O_2N.C_7H_7Br$ , crystallises in colourless silky needles, melts at  $130^\circ$  (uncorr.), and is readily soluble in water and alcohol, insoluble in ether. When heated in aqueous solution, it yields *quinolinebenzylbetaine*,  $C_{10}H_6O_2N.C_7H_7 + 3H_2O$ , crystallising in colourless quadratic tables. These melt at  $83-84^\circ$ , re-solidify on further heating at  $110^\circ$ , and again melt with decomposition at  $190^\circ$ . It is readily soluble in water and alcohol, insoluble in ether and chloroform. The aqueous solution has a neutral reaction, and gives a red coloration with ferric chloride. Hydrochloric acid converts the betaine into a substance identical with the additive compound formed by cinchonic acid and benzyl chloride. By the action of soda on either the betaine or the compound of benzyl bromide with cinchonic acid, a new acid is formed which has not been obtained in a pure state.

Quinolineparasulphonic acid does not form additive products when heated with alkyl haloid compounds, its silver salt however reacts with these compounds, forming quinoline sulphobetaines; silver quinolineparasulphonate and ethyl bromide yield a crystalline compound of the formula  $C_9NH_5SO_3Et + 2H_2O$ . A. J. G.

**$\beta$ -Naphthoquinolinesulphonic Acid.** By C. GENTIL (*Ber.*, **18**, 201—202).—In order to prepare this compound,  $\beta$ -naphthylamine-sulphonic acid is heated with glycerol, nitrobenzene, and concentrated sulphuric acid. The excess of nitrobenzene is expelled by steam, the residue converted into barium salt, filtered from the barium sulphate, and the barium precipitated by the addition of sulphuric acid.  *$\beta$ -Naphthoquinolinesulphonic acid*,  $SO_3H.C_{10}H_5 : C_3NH_3 + Aq$ ? crystallises in groups of slender white needles, dissolves sparingly in alcohol and cold water, but readily in hot water. The barium salt,  $(C_{13}H_8N.SO_3)_2Ba$ , when dried over sulphuric acid, contains 12.82 per cent. water, and the silver salt,  $SO_3Ag.C_{10}H_5 : C_3NH_3$ , 15.00 per cent. (3.5 mols.  $H_2O$ ).  *$\beta$ -Hydroxynaphthoquinoline*,  $OH.C_{10}H_5 : C_3NH_3$ , obtained by fusing the acid with potash, does not melt at  $250^\circ$ , but sublimes with partial decomposition; it yields a sparingly soluble platinochloride which crystallises in yellow needles. A. K. M.

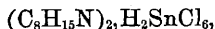
**Hydro-compounds of Cinchonic Acid.** By H. WEIDEL and K. HAZURA (*Monatsh. Chem.*, **5**, 643—655).—One of the authors has already shown (*Abstr.*, 1882, 531) that when methyltetrahydrocinchonic acid is heated at  $100^\circ$  it is converted into an oil; further investigation has shown this substance to be *methyltetrahydrocinchonic anhydride*,  $(C_9H_9NMe.CO)_2O$ . It is an almost colourless oil, boiling at  $297-299^\circ$ , under 744.3 mm. pressure; it is decomposed by exposure to the air. When heated with hydrochloric acid at  $150^\circ$ , it yields methyl chloride, and the *hydrochloride of tetrahydrocinchonic acid*, thus:  $C_{22}H_{24}N_2O_3 + H_2O + 4HCl = 2MeCl + 2C_{10}H_{11}NO_2.HCl$ . When heated at  $150^\circ$  with solutions of caustic alkalis, the anhydride yields salts of *homohydrocinchonic acid*, the free acid is obtained by

decomposing the product of the reaction with sulphuric acid. It crystallises from ether and light petroleum in aggregations of white pearly scales, melting at  $125^{\circ}$ , and having the composition  $C_{11}H_{13}NO_2$ . It is an extremely feeble acid, but forms well-defined crystalline salts with acids. Its *hydrochloride*,  $C_{10}H_{10}MeNO_2 \cdot HCl + H_2O$ , crystallises in large colourless crystals, of the prismatic system,  $a : b : c = 0.9314 : 1 : 2.07$ ; observed faces, 001, 012, 111. The *methiodide*,  $C_{10}H_{10}MeNO_2 \cdot MeI + H_2O$ , crystallises in large, transparent, slightly yellow crystals, belonging to the monoclinic system; when treated with silver oxide, it yields a compound of the formula  $C_{10}H_9Me_2NO_2 + H_2O$ , the aqueous solution of which evaporated in an atmosphere of hydrogen forms small, colourless shining crystals, extremely soluble in water.

Homohydrocinchonic acid heated at  $170^{\circ}$  with concentrated sulphuric acid yields *lepidinesulphonic acid*; this crystallises from hot water in yellowish, flexible lustrous leaflets, having the composition  $C_{10}H_8N \cdot HSO_3$ . The production of this compound indicates that in homohydrocinchonic acid one methyl-group is contained in the hydropyridine nucleus.

P. P. B.

**The Conine Group.** By A. W. HOFMANN (*Ber.*, 18, 109—131).—When conine hydrochloride or hydromide is acted on by bromine, an additive product ( $C_8H_{17}N \cdot HBr, Br_2?$ ) is obtained, and this, when treated with soda solution, yields the compound  $C_8H_{16}NBr$  as an almost colourless, heavy liquid of penetrating odour. The same compound is obtained when bromine (1 mol.) is mixed with a 5 per cent. solution of sodium hydroxide (1 mol.), which is then well cooled, and conine (1 mol.) added. By the action of sulphuric acid on the product, hydrogen bromide is eliminated and  $\alpha$ -coniceine (this vol., p. 401) formed; whilst if the change is effected by means of an alkali,  $\gamma$ -coniceine is produced differing from both the  $\alpha$ - and  $\beta$ -compounds. In order to obtain  $\alpha$ -coniceine, the bromine-derivative is gradually added to concentrated sulphuric acid, and the colourless solution obtained slowly heated to  $140^{\circ}$ , and maintained at this temperature as long as bromine and hydrobromic acid are evolved, after which the acid is neutralised by the addition of alkali. To obtain  $\gamma$ -coniceine, a dilute solution of conine hydrochloride or hydrobromide (1 mol.) is mixed with bromine (1 mol.), and the product treated with a dilute solution of an alkali (2 mols.). The whole is heated for about half an hour on a water-bath. As the liquid cools, a little tribromhydroxyconine hydrobromide separates, whilst  $\gamma$ -coniceine and unaltered conine remain in solution; these two bases may be separated by means of stannic chloride, which yields a well-crystallised double salt with  $\gamma$ -coniceine. This base forms a colourless transparent liquid lighter than water, in which it dissolves sparingly with a strongly alkaline reaction; its odour closely resembles that of conine, whilst as a poison it appears to act even more powerfully than the latter substance. It remains liquid at  $-50^{\circ}$  (distinction from the  $\alpha$ -compound), and boils at  $173^{\circ}$ ; its salts are crystalline, but deliquescent (distinction from  $\beta$ -coniceine). The platinochloride,  $(C_8H_{15}N)_2 \cdot H_2PtCl_6$ , aurochloride,  $C_8H_{15}N \cdot HAuCl_4$ , and the stannichloride,



are also described.  $\gamma$ -Coniceïne is shown to be a secondary amine by its behaviour with acetic anhydride and by its not yielding an isonitrile; the acetyl-derivative,  $C_8H_{14}N\text{Ac}$ , is insoluble in water and in hydrochloric acid; it boils at  $252\text{--}255^\circ$ . When an alcoholic solution of the base is treated with methyl iodide and sodium hydroxide, and the iodide of the ammonium base thus formed is converted into the corresponding chloride, and then into the platinochloride, a salt is obtained which is not the expected compound,  $(C_8H_{14}MeNMe)_2PtCl_6$ , but has the composition of the methylammonium salt of a dimethylated oxyconine,  $(C_8H_{15}Me_2NOMe)_2PtCl_6$ ; the aurochloride has the formula  $C_8H_{15}Me_2NOMe, AuCl_4$ . When the hydroxide of the ammonium base is distilled, it yields dimethyloxyconine,  $C_8H_{15}Me_2NO$ , and methyl alcohol,  $C_8H_{15}Me_2NOMe.OH = C_8H_{15}Me_2NO + MeOH$ , also trimethylamine and a compound,  $C_8H_{14}O : -C_8H_{15}Me_2NOMe.OH = C_8H_{14}O + H_2O + NMe_3$ . Dimethyloxyconine forms a colourless liquid of characteristic odour, is sparingly soluble in water, and boils at  $225\text{--}226^\circ$ ; the aurochloride has the composition  $C_{10}H_{21}NO, HAuCl_4$ . The compound  $C_8H_{14}O$  is an oil lighter than water and boils at  $165\text{--}166^\circ$ ; it has a penetrating odour, recalling that of peppermint-oil.

*Tribromoxyconine hydrobromide*,  $C_8H_{14}Br_3NO, HBr$ , which is produced in the conversion of conine into  $\gamma$ -coniceïne (see above), may be obtained as the chief product if a larger proportion of bromine be employed:  $C_8H_{17}N + 4Br_2 + H_2O = C_8H_{14}Br_3NO, HBr + 4HBr$ . The platinochloride,  $(C_8H_{14}Br_3NO)_2, H_2PtCl_6$ , and aurochloride,  $C_8H_{14}Br_3NO, HAuCl_4$ , are described; the free base is a heavy oil of penetrating odour; the hydrochloride, sulphate, and nitrate are sparingly soluble and crystallise well. Tribromhydroxyconine is very unstable and rapidly changes with production of the hydrobromide and of a base,  $C_8H_{13}Br_2NO$ . By the action of tin and hydrochloric acid on the hydrobromide,  $\gamma$ -coniceïne is produced together with other bases. *Dibromoxyconiceïne*,  $C_8H_{13}Br_2NO$  (see above), is a heavy oil having an odour resembling that of conine; it is unstable in the free state, but does not decompose in acid solution; the platinochloride,  $(C_8H_{13}Br_2NO)_2, H_2PtCl_6$ , is sparingly soluble. When dibromoxyconiceïne is acted on with tin and hydrochloric acid, *oxyconiceïne*,  $C_8H_{15}NO$ , is formed. It is a colourless liquid, has an odour somewhat resembling that of conhydrine, and distils between  $210^\circ$  and  $220^\circ$ ; its hydrochloride crystallises in needles; the aurochloride has the formula  $C_8H_{15}NO, HAuCl_4$ . Besides this base, a high boiling basic substance (*coniceidine*) is also produced in the last-mentioned reaction; its hydrochloride crystallises in small plates, sparingly soluble in water, readily in hydrochloric acid and in alcohol. Coniceidine,  $C_{16}H_{26}N_2$ , may also be prepared by boiling oxyconiceïne with alcoholic potash:  $2C_8H_{15}NO = C_{16}H_{26}N_2 + 2H_2O$ . The platinochloride,  $C_{16}H_{26}N_2, H_2PtCl_6$ , forms almost insoluble stellate groups of needles. The free base melts at  $55\text{--}56^\circ$ , and boils above  $300^\circ$  with decomposition. From its formula it appears to be a homologue of nicotine. A. K. M.

**New Alkaloids of Cuprea Bark.** By B. H. PAUL and A. J. COWNLEY (*Pharm. Journ.* [3], 15, 221—222, and 401—402).—The authors regarding homoquinine as a distinct alkaloid and not as a modi-

fication of quinine (Abstr., 1884, 1385), repeated Hesse's experiment described in the Abstract referred to; they found one treatment with soda sufficient to effect the change, but that the quantity of quinine obtained was considerably less than the amount of homoquinone employed. Examination of the soda solution disclosed the remainder of the homoquinine, in the form of a new alkaloïd which they call *cupreïne*. It crystallises from its ethereal solution in rhombic plates, different from those of homoquinine. No quinine is obtained by digesting it with soda; but the soda solution, on exposure and evaporation, sets to a jelly. In a quantitative experiment, a specimen of homoquinone yielded 62.37 per cent. cupreïne and 37.63 per cent. quinine. Synthetical experiments, wherein mixed ethereal solutions of quinine and cupreïne were allowed to evaporate slowly, resulted in the production of homoquinine. The authors have compared various salts of the three alkaloïds, quinine, cupreïne, and homoquinine, and find a marked difference in their characteristics:—

	Cupreïne.	Homoquinine.
Sulphate .....	Forms tufts of radiating acicular crystals.	More soluble than cupreïne salt, forms slender needles sometimes in stellate groups.
Acid sulphate.....	Less soluble than homoquinine salt; crystals as above.	On evaporation forms a gelatinous residue.
Hydrochloride ....	Bunches of long needles with glassy lustre.	Amorphous, more soluble than cupreïne salt.
Oxalate .....	Amorphous, more soluble than homoquinine salt.	Delicate needles, opaque when dry.
Tartrate .....	More soluble than homoquinine salt.	Very sparingly soluble.
Hydriodide .....	Distinctly crystalline.....	Resinoid.

Copious reference is made to Hesse's paper (this vol., p. 276).

D. A. L.

**Brucine.** By O. DE CONINCK (*Compt. rend.*, **99**, 1077—1079).—Heavy quinoline, obtained by the action of an excess of potash on brucine, contains a small quantity of tetrahydroquinoline (Abstr., 1882, 414). Its platinochloride forms an orange-red crystalline powder, which rapidly changes into a modified salt or is completely reduced; no aurochloride could be obtained. The free base or a strongly acid solution of the hydrochloride almost instantly reduces gold chloride, ferric chloride, or stannic chloride. In these properties tetrahydroquinoline closely resembles the pyridic dihydrides.

It would seem that there is a gradation in the stability of the hydrogen combined with pyridic or quinolic alkaloids. Pyridic dihydrides are very unstable and have great reducing power; quinolic tetrahydrides have the same properties in a somewhat less marked degree; pyridic hexahydrides are not reducing agents and are much more stable, but they contain a certain number of hydrogen-atoms which can easily be removed from the molecule.

The occurrence of tetrahydroquinoline in the crude quinoline from

brucine shows that this alkaloïd, like cinchonine, contains in its molecule a quinolic tetrahydride. C. H. B.

**Brucine.** By A. HANSEN (*Ber.*, 18, 293—294).—A reply to Shenstone (this vol., p. 276).

**Derivatives of Dimethylpiperidine.** By A. LADENBURG (*Ber.*, 18, 55).—With reference to Merling's work on "Bromosubstitution-derivatives from Dimethylpiperidine," the author calls attention to his own work with iodine in a similar direction (*Abstr.*, 1882, 534 and 983), and expresses the opinion that Merling will not in this way do much towards elucidating the relationship between tropine and piperidine. L. T. T.

**Cocaïne.** By E. MERCK (*Pharm. J. Trans.* [3], 15, 426—428).—The paper refers to the use of cocaïne in surgery. It produces local anæsthesia; the fatal dose is small for the lower animals, but considerable for human beings. It has been employed successfully for ophthalmic and dental purposes. Dropping a 2 per cent. solution into the eye causes an entire loss of feeling, lasting for 10 minutes; whilst, if applied to a tooth, any operation may be performed on it without causing pain. The hydrochloride, salicylate, and citrate have been employed, but doubtless other cocaïne salts are equally efficient. D. A. L.

**Hymenodictyonine, the Bitter Principle of Hymenodictyon Excelsum.** By W. A. H. NAYLOR (*Pharm. Journ.* [3], 15, 195—196).—The author has continued his experiments on this substance, and has taken special precautions in its preparation. In addition to facts already published (*Abstr.*, 1883, 1141), he now adds, that by very slow evaporation of the ethereal solution, the alkaloïd has been obtained in acicular crystals; also that on treatment with concentrated sulphuric acid a solution is obtained yellow to wine-red by transmitted, and showing bronze fluorescence by reflected light, sulphurous acid being at the same time given off. From numerous quantitative experiments, he concludes that this alkaloïd is a tertiary diamine of the composition  $C_{23}H_{40}N_2$ . Its hydrochloride,  $C_{23}H_{40}N_2 \cdot 2HCl$ , its platinochloride, and the diethyl-derivative have been examined; also the iodide of the latter,  $C_{23}H_{40}Et_2N_2I_2$ , which forms rosettes of long needles, soluble in hot alcohol, and the platinochloride,  $C_{23}H_{40}Et_2N_2 \cdot PtCl_6$ , which forms large crystals scarcely soluble in alcohol. D. A. L.

**Active Constituents of Nandina Domestica.** By J. F. EIJKMAN (*Chem. Centr.*, 1884, 779—780).—This plant belongs to the family Berberidaceæ, and grows in China and Japan. Its leaves are said to possess intoxicating properties, or at least to act as an emetic. The author has isolated from the root-bark an alkaloïd, *nandinine*, an amorphous white powder; it assumes a dark colour when in aqueous solution, or on exposure to a moist atmosphere. Nandinine is soluble in the ordinary solvents, does not yield crystalline salts, is poisonous, and gives the ordinary reactions of alkaloïds. It gives a

reddish-violet solution with strong sulphuric acid, which changes to blue on addition of a small quantity of nitric acid. Other oxidising substances, even ferric chloride, produce a green or blue colour, whilst selenic or telluric acid give rise first to a green, and then to an indigo-blue coloration. Nandinine platinochloride gives a splendid blue colour with sulphuric acid, whilst with chlorine or bromine-water it gives a fine green.

The numbers obtained by analysis agree with the formula  $C_{19}H_{19}NO_4$ , according to which nandinine would be the homologue of hydroberberine,  $C_{20}H_{21}NO_4$ . Berberine seems to be also present in the plant.

H. W.

**New Base occurring in the Animal Organism.** By A. KOSSEL (*Ber.*, 18, 79—81).—Whilst continuing his researches on nucleïn and its decomposition-products, guanine and hypoxanthine (*Abstr.*, 1883, 759; 1884, 97, and this vol., p. 286, &c.), the author has isolated from the pancreatic gland of the ox, a new base,  $C_5H_5N_5$ , to which he gives the name *adenine*. It crystallises in needles which decompose before melting. It is soluble in alcohol and boiling water, and the aqueous solution has a neutral reaction. The *sulphate*,  $(C_5H_5N_5)_2 \cdot H_2SO_4$ , crystallises with  $2H_2O$ ; the *hydrochloride*, *platinochloride*, and *nitrate* are also crystalline. It resembles hypoxanthine in its behaviour with silver nitrate. The author has also detected this base in the spleen of the ox and in pressed yeast.

L. T. T.

**Ptomaïnes from Fish.** By O. BOCKLISCH (*Ber.*, 18, 86—89).—In a pamphlet on "Ptomaïnes" (Berlin, 1885), Brieger has lately given the results of his researches on the putrefaction alkaloids obtained from cod-fish, &c. He obtained neuridine,  $C_5H_{14}N_2$ , ethylenediamine, muscarine, and gadinine,  $C_7H_9NO_2$ . The author is carrying out similar researches with fresh-water fish. By the putrefaction of the perch, he obtained neuridine, dimethylamine, trimethylamine, a base apparently isomeric with trimethylamine, and traces of other basic substances. The base just mentioned resembles muscarine in properties, and is probably identical with a ptomaïne obtained by Brieger from the human corpse. It forms a *platinochloride* crystallising in needles, and a hydrochloride which yields non-deliquescent colourless needles. These results seem to show that the alkaloids formed during the putrefaction of fresh-water fish are different from those obtained under similar circumstances from salt-water fish.

L. T. T.

**Preparation of Hæmin.** By M. SHALFEIEF (*J. Russ. Chem. Soc.*, 1885, 30).—The following method is recommended for preparing considerable quantities of Teichmann's hæmin crystals, without previously submitting the blood to any particular treatment:—To 1 vol. of glacial acetic acid heated to  $80^\circ$ , 1 vol. of ox blood, which has been defibrinated and filtered through cloth, is added, and the whole again heated to  $80^\circ$ ; on cooling abundance of crystals are deposited; these are repeatedly washed with water, collected, and again washed on the filter successively with water, alcohol, and ether. The crystals, which are oblong rhomboidal plates, are brownish-red by

transmitted, and dark violet-blue with a metallic lustre by reflected light.

The various forms of hæmin crystals observed under the microscope, when blood is treated by Teichmann's method, are due to variations in the relative quantities of blood and acetic acid, so that any of the forms hitherto described may be obtained by varying the proportions of acid and blood. The formation of the crystals is also affected by temperature; if heated above  $80^{\circ}$ , the crystalline deposit is either diminished, or is redissolved and does not separate again on cooling.

The yield of hæmin crystals from 1 litre of blood by the method described is never less than 5 grams, generally about 83—90 per cent. of the amount theoretically calculated. When the blood was partially decomposed, or when the acid had been heated to  $90$ — $95^{\circ}$ , the crystals deposited were extremely small, but the supernatant liquid appeared almost colourless, so that the separation of the colouring matter must be complete under these conditions.

A. T.

**Crystallographic form of Hæmin.** By A. LAGORIO (*J. Russ. Chem. Soc.*, 1885, 35).—Hæmin crystals belong to the triclinic system, the principal combinations being:  $0P$ ,  $\infty\bar{P}\infty$ ,  $\bar{P}'\infty$  or  $\infty\bar{P}\infty$ ,  $\infty\bar{P}\infty$ ,  $\bar{P}'\infty$ , sometimes  $\infty\bar{P}\infty$ ,  $\infty\bar{P}\infty$ ,  $0P$ . The angles measured are:  $0P$ ,  $\infty\bar{P}\infty = 121^{\circ}$ ,  $\infty\bar{P}\infty$ ,  $\infty\bar{P}\infty = 74^{\circ}$ ,  $\infty\bar{P}\infty$ ,  $0P = 112^{\circ}$ , and  $\infty\bar{P}\infty$ ,  $\bar{P}'\infty = 147^{\circ}$ . The crystals are pleochroic in a high degree.

A. T.

**Filtration of Albumin Solutions.** By J. W. RÜNEBERG (*Pflüger's Archiv*, 35, 54—67).—A reply to Regézy (*ibid.*, 30, 544; compare also this vol., p. 405).

**Putrefaction of Albumin and Formation of Skatole and Indole.** By E. and H. SALKOWSKI (*Zeit. Physiol. Chem.*, 8, 417—466).—The occurrence of considerable amounts of indican, phenol, and benzoic acid in the urine in a case of peritonitis, led the authors to suppose that benzoic acid was formed by putrefaction in the intestinal canal. The analogy with the larger herbivora, in whose intestines food remains for long periods, and whose urine is characterised by the presence of those three substances, cannot be overlooked. The authors undertook some experiments on the results of the putrefaction of albuminous substances with a view to solve the question.

The substances selected for the experiments were blood fibrin, lean muscle, and serum albumin. The manner of procedure is thus described:—The material—say horse flesh—weighing 2 kilos., was very finely chopped and placed in a large flask containing 8 litres of water at  $40$ — $42^{\circ}$ ; to this 200—240 c.c. of saturated solution of sodium carbonate was added, a quantity found sufficient to maintain the alkalinity of the solution to the end of the experiment; the mixture is then seeded with a putrefactive solution prepared by rubbing lean flesh with water in a mortar, and digesting it with sodium carbonate to decidedly alkaline reaction, in an incubator at  $40$ — $42^{\circ}$  for two hours, at the end of which time it is in a putrid state and swarming with organisms; some few c.c. of this preparation are added to the large flask, which is then corked loosely and placed in the incubator; when gas ceases to be evolved, the cork is driven in.



more firmly. The authors prefer this inoculation to spontaneous decomposition, as the process can be more sharply watched. With flesh, the addition of nutritive salts is unnecessary. When the mixture had remained a fixed time in the incubator, it was distilled, without filtration or addition of acids, until the residue was about 1—1½ litre; in the strongly ammoniacal distillate indole and skatole were found and nearly all the phenol, also traces of fatty and aromatic acids in combination with ammonia, but the greater part of those acids remained in the residue as sodium salts. At the commencement of ebullition, the steam carried over a small quantity of a pale yellow oil which sank under water, and had the highly characteristic odour of mercaptan. Another substance of the nature of indole, but differing in certain reactions, was also found, the quantities of both being too small for full examination. One of them is probably the substance described by Brieger (Abstr., 1879, 806).

The separation of indole and skatole from the distillate was effected by agitation with ether, after acidifying with hydrochloric acid. Any phenols or acids accompanying the indole and skatole are removed by agitating with soda, &c.

The authors describe an exhaustive series of experiments, in which they submitted various substances to putrefaction for different periods, and estimated the indole and skatole formed, comparing this with the quantities of dissolved albumin contained originally in the substance.

The samples containing most skatole were those from flesh or flesh fibrin, but in other cases the indole obtained from those substances contained merely traces of skatole. The authors account for the difference by assuming that the organisms with which the substance was inoculated contained more of the skatole ferment in one case, and of the indole ferment in the other.

When the authors compare their researches with those of previous investigators on the origin of skatole, they find serious differences. Brieger looks on skatole as a constant product of putrefaction, but the authors believe that both skatole and indole have a common origin, and replace each other in varying proportions, owing to circumstances as yet but partially understood. In active putrefaction, the time necessary for the appearance of indole is very short—with preparations of flesh it required but two days. The indole group, according to the authors, forms a much greater proportion of the molecule of albumin than is generally supposed, and appears to differ in amount in different albuminous substances, nor does it appear to be a direct product of putrefaction, but the result of bacteria working on an intermediate substance which is at present unknown. The experiments of Odermatt, Nencki, and Brieger have shown that the quantity of indole diminishes as the solution of the substance is kept for a longer period, but the authors did not find it so in their experiments; they note, however, that the others employed open vessels, whilst they used closed flasks. They account for the diminution by a process of oxidation, and believe that dilution of the solution has also an effect in this direction. Hoppe-Seyler has shown that putrid solutions, when supplied with sufficient oxygen, do not develop either indole or skatole.

J. F.

**Skatolecarboxylic Acid, a Product of the Putrefaction of Albumin.** By E. and H. SALKOWSKI (*Zeit. Physiol. Chem.*, 9, 8—22).—In addition to indole and skatole, the putrefaction of albumin yields other substances, amongst them skatolecarboxylic acid,  $C_{10}H_9NO_2$  (compare Abstr., 1881, 175). It forms small leaflets easily soluble in alcohol and ether, sparingly in water; they dissolve in hot water, but on cooling, the greater part is again precipitated, the small portion left in solution reacting strongly acid. The acid is monobasic; the melting point is about  $164^\circ$ . On further heating it is decomposed, evolving carbonic anhydride, and yielding a sublimate of pure skatole. When the acid is mixed with a few drops of hydrochloric acid, a very dilute ferric chloride solution added, and the mixture boiled, a cherry-red colour is produced.

The authors have found this acid in 15 carefully conducted experiments, and are inclined to regard skatolecarboxylic acid as the mother-substance of skatole, although the resistance of the material to bacteria appears contradictory to the hypothesis.

The fact that the acid is inodorous leads to the belief that it is derived from the ferment of trypsin, but against this opinion there are also objections.

J. F.

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## Physiological Chemistry.

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**Relative Digestibility of Fish in Gastric Juice.** By R. H. CHITTENDEN and G. W. CUMMINS (*Amer. Chem. J.*, 6, 318—332).—In this paper the authors have attempted to obtain some positive results as to the relative digestibility of the more common edible species of fish, comparing it at the same time with the digestibility of beef, veal, lamb, &c. Artificial digestion was the method employed, a solution of 5 grams of commercial “pure pepsin” in a litre of dilute hydrochloric acid of 0.2 per cent. strength forming the digestive mixture, a fresh quantity of which was prepared for each experiment. The flesh was freed as much as possible from tendons, fat, skin, and bones, and finely divided by chopping. The solid matter in every sample was determined, and then two portions, of 20 grams each, weighed out to determine the digestibility. These were heated in a steam-bath for 30 minutes, then placed each in a beaker containing 200 c.c. of the standard gastric juice, and finally heated in a bath at 38—40° for 22 hours, with occasional stirring. The quantity digested was determined by making up the mixture with water to 250 c.c., filtering and evaporating to dryness 50 c.c. of the filtrate, and weighing the residue. This latter process was found to be much more convenient than filtering and weighing the undigested residue, as it was almost impossible to wash the latter free from peptones, owing to its gelatinous condition. In each case a duplicate analysis was made.

The results of the analyses, given in the appended table, show great divergence in the results obtained from different samples of the

	Solids, per cent.	Digestibility. Beef = 100.
Beef.....	25·12—26·03	100·00
Veal .....	24·29—24·96	94·89
Mutton.....	30·84	92·15
Lamb.....	29·87	87·93
Spring chicken (light meat) .....	26·64	86·72
„ „ (dark meat) .....	26·70	84·42
Lake white .....	25·56	94·78
Shad .....	31·33	90·09
„ (light meat) .....	30·38	97·25
„ (dark meat) .....	32·63	87·32
Salmon .....	31·06	92·29
„ .....	31·50	89·80
Tantog .....	20·60	88·13
Porgie .....	22·56	87·03
Blue fish .....	19·84	88·69
„ .....	19·46	73·44
Mackerel .....	25·51	86·24
Halibut .....	20·28	85·51
Flounder .....	23·04	85·32
Sea bass .....	21·17	84·01
Pike .....	19·63	82·99
Haddock .....	18·24	82·50
Herring .....	24·49	82·34
Striped bass .....	20·73	80·99
Red snapper .....	22·09	81·65
Trout, brook.....	19·58	78·45
Sea robin .....	21·87	78·03
White perch .....	19·69	72·94
Fresh cod .....	18·29	72·39
Eel.....	21·78	71·82
Flat fish .....	17·15	66·89
Lobster (young) .....	21·75	87·81
„ (large female) .....	21·29	79·06
„ (large male).....	20·76	69·13
Crab .....	23·57	67·13
Frog's legs .....	17·86	80·46

same species of fish, and point to the conclusion that there are other conditions, such as age, sex, &c., which affect the digestibility of their flesh, and which must be taken into account in generalising from these experiments; examples of this are seen in the three experiments on the lobster. Generally speaking, the white flesh is more easily digestible than red or dark flesh. The low digestibility of the flesh of fresh cod is noteworthy.

The whole of the flesh experimented on was steam-cooked. Raw meat, of whatever kind, was found to be much more easily digestible, as experiments with raw and cooked beef and blue fish showed.

J. K. C.

**Physiological Action of Cocaine.** By GRASSET and JEANNEL (*Compt. rend.*, 100, 364—366).—Cocaine hydrochloride was administered to monkeys and dogs by hypodermic injection in different quantities. The results lead to the following conclusions:—Cocaine produces in monkeys violent attacks of convulsions. Chloral is antagonistic to cocaine both in respect to its effect on the excitomotor functions and the temperature of the body. The thermal effect of cocaine seems to be different in the case of monkeys and dogs. Antipyrine does not seem to be antagonistic to cocaine so far as thermal effect is concerned (see p. 565). C. H. B.

**Physiological Effect of Cinchonamine Sulphate.** By G. SÉE and BOCHEFONTAINE (*Compt. rend.*, 100, 366—368).—The effects produced by cinchonamine sulphate are progressive weakening of the physiological activity of the central nervous system, weakening and slackening of the movements of the heart, and, in mammalia only, indistinct convulsions. Large doses rapidly produce death by stoppage of the heart in diastole, both in batrachians and mammalia. Atropine does not restore movements of the heart which have been arrested by cinchonamine. The toxic action of cinchonamine is about six times as great as that of quinine, cinchonidine, or cinchonine.

C. H. B.

**Origin of the Fibrin Ferment.** By L. C. WOOLDRIDGE (*Proc. Roy. Soc.*, 36, 417—420).—The fibrin ferment which appears in shed blood is generally supposed to arise from the cellular elements of blood, from the white or some special kind of other corpuscles, either by their discharge of the ferment into the blood, or by their actual disintegration. Although this may be one source of fibrin ferment, yet in this paper evidence is brought forward to show that it may make its appearance in blood plasma perfectly free from cells, and it must thus arise from some constituents of the plasma. This ferment does not pre-exist in normal plasma, although it may make its appearance even in the absence of all cellular matter.

V. H. V.

**Action of a Secretion obtained from the Medicinal Leech.** By J. B. HAYCRAFT (*Proc. Roy. Soc.*, 36, 478—487).—It is well known that the blood flowing from a leech bite is not readily stopped, whilst the blood within the leech remains fluid for an indefinite time, and when ejected has lost its power of coagulating. In this investigation it is shown that the leech secretes from the mouth a liquid which destroys the blood ferment, without producing any other observable change. Attempts made to isolate the active principle of the liquid have hitherto been unsuccessful, owing to its insolubility in the more common menstrua. When this liquid is injected into an animal, such as the rabbit or dog, it produces but slight constitutional disturbance, and is eliminated by the kidneys; it has no effect on crustacean blood. It does not curdle milk, slightly hastens the clotting of myosin, and hastens rigor mortis. The active principle is not a ferment, inasmuch as it retains its activity after boiling.

V. H. V.

**The Proteids of Serum.** By W. D. HALLIBURTON (*Proc. Roy. Soc.*, 37, 102—107).—This investigation deals particularly with experi-

ments on the coagulation by heat, and the action of certain salts on the proteïds of blood serum of man and of various animals, and of so-called serous effusions such as the hydrocele, pleuritic, ascitic, and parovarian fluids. The most important results are as follows: (1) The albumin of serum consists of three separate proteïds, coagulating at temperatures of 73°, 77°, and 84°, which may provisionally be called 1, 2, and 3 serum albumin. In certain animals only two of these are present; (2) The precipitates described by Fredericq as occurring in serum at temperatures below 70° do not occur; (3) the albumins of serum can be completely precipitated, after saturation with magnesium sulphate and removal of the serum globulin, by saturation with sodium sulphate; (4) potassium acetate added in excess to a solution of the proteïd completely precipitates it without coagulation. V. H. V.

**A Peptone-like Constituent of the Cell Nucleus.** By A. KOSSEL (*Zeit. Physiol. Chem.*, 8, 511—515).—The blood-corpuscles of birds offer considerable facilities for chemical examination; most other animal organs which are subjected to analysis consist of various tissues, but we have in the red corpuscles properly isolated a histologically uniform substance, which preserves the typical character of the cell, and is distinguished from the cells of the tissues by the solubility of the cell-wall in water, the insoluble residue consisting mainly of the nuclei of the cell, mixed with a filamentous substance—the stroma.

The following experiments were made on the blood of a goose. The corpuscles were isolated in the usual way, dissolved in water to which a little ether was added, and the undissolved substance washed with water until completely decolorised. It has been shown by Plósz that this matter is very rich in nucleïn, it is very light and easily compressed, it contracts in alcohol, and much more so on addition of a few drops of hydrochloric acid to water in which it is suspended. Previous investigations have convinced the author that there is another body existing in chemical combination with the nucleïn, as extraction with dilute acid isolates a substance which belongs to the class of bodies called A-peptones by Meissner, propeptones by Schmidt, and albumoses by Kühne. This compound is soluble in water, and as it is not extracted by water previous to treatment with acid, it must either be formed by the action of the acid, or liberated by it from its combination. The author names this substance *histon*; it is procured in the following manner: salt is added to the acid solution previously mentioned, the abundant precipitate collected, washed with acid containing salt, thrown into water and subjected to dialysis—the salt diffuses into the outer vessel whilst the substance dissolves in the dialyser. The neutral solution of *histon* is precipitated by more or less perfect saturation with ammonium sulphate or chloride, magnesium sulphate, common salt, or sodium carbonate. A precipitate is also produced by ammonia, lime-water, sodium hydroxide, and nitric acid. The solution is not precipitable by calcium chloride, mercuric chloride, normal or basic lead acetate, sodium phosphate, or by acetic or sulphuric acids. The *concentrated* solution is precipitated by alcohol, and the precipitate is easily soluble in water; on boiling there is no coagulation. Copper

sulphate and sodium hydroxide solution in the cold produce a red colour, the so-called peptone reaction; prolonged heating with baryta-water yields leucine and tyrosine.

The behaviour of histon with ammonia is peculiar, a few drops of aqueous ammonia added to the neutral solution produces a heavy precipitate; when filtered, the filtrate does not give the peptone reaction, and the precipitate is quite insoluble, possessing all the properties of an albuminoid. This method may be employed as a means of separating peptones from albuminous substances. J. F.

**Inorganic Constituents of Muscle.** By G. BUNGE (*Zeit. Physiol. Chem.*, 9, 60—62).—The author has recently made some very careful analyses of the ash of beef, freed as much as possible from fat, tendons, veins, &c., and as many physiological conclusions have been drawn from previous analyses, he publishes the figures: I, with which he compares; II, those of fat beef—analysed on a previous occasion. The results are given in parts per 1000:—

	K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	Cl.	SO <sub>3</sub> .	S.
I.	4.654	0.770	0.086	0.412	0.057	4.674	0.672	—	—
II.	4.160	0.811	0.072	0.381	—	4.580	0.709	0.010	2.211

With regard to the tissue alterations taking place during a flesh diet, it is worthy of remark that the sulphuric acid which is formed by the separation and oxidation of the albuminoids of muscle, is sufficient to saturate all the basic constituents. As much as 85 per cent. of the sulphur contained in the food passes away in the urine as sulphuric acid. The muscles contain considerable quantities of phosphorus and chlorine, but there is no fear of free acid being formed, owing to the simultaneous production of ammonia, creatinine, and other basic substances. J. F.

**Soaps as Constituents of Blood Plasma and Chyle.** By F. HOPPE-SEYLER (*Zeit. Physiol. Chem.*, 8, 503—507).—This paper is a reply to the assertions of Lebedeff and Röhrig that neither blood nor chyle contains alkali salts of the fatty acids. The presence of calcium and magnesium combinations in these fluids does not necessarily exclude that of alkaline soaps; it is easy, without any complex operation, to obtain several grams of soap from the blood serum of oxen and horses.

It is well known that sodium carbonate is always present in blood plasma, chyle, and lymph, and the use of sodium carbonate in washing, to prevent the precipitation of lime and magnesia soaps is also well known.

The presence of a soda soap in the serum of blood and of chyle is thus shown: the fluids are precipitated with 3 or 4 vols. of strong alcohol, filtered, and evaporated to a syrup at a temperature not exceeding 55°, extracted with ether free from both alcohol and water; the residue treated with absolute alcohol, filtered, and evaporated at 55° to a clear syrup; this when dissolved in a little hot water, gives all the reactions of soap.

Blood serum of the ox, horse, and dog contains 0·05 to 0·12 per cent. of the fatty acids of soap; human chyle 0·23 per cent. of soap and 0·723 per cent. fat; and blood serum in a case of pneumonia, 0·662 fatty acids of soap. The origin of soap in those fluids is as yet unaccounted for.

J. F.

**Assimilation of Iron.** By G. BUNGE (*Zeit. Physiol. Chem.*, **9**, 49—59).—Many physiologists believe that the human organism possesses the power of synthesising hæmoglobin from albumin and inorganic combinations of iron, but recent experiments on animals have shown that the introduction of iron salts into the blood is followed by symptoms of poisoning similar to those with arsenic.

The questions which the author proposes to solve are the form in which, under normal conditions, iron is absorbed and assimilated, and the manner in which hæmoglobin is formed. The subjects of experiment were milk and yolk of egg; the former, as being the exclusive food of the young mammalia, must contain the material of hæmoglobin, whilst egg-yolk must form it during the process of incubation, without access to external sources. Milk is difficult to examine, the quantity of iron contained being so small; egg-yolk is richer, and it is easier to isolate the metal. The author describes the method by which he obtains from the yolk a substance which he calls hæmatogen; the mean of nine analyses show its composition to be—

C.	H.	N.	S.	P.	Fe.	O.
42·11	6·08	14·73	0·55	5·19	0·29	31·05

He cannot say whether it is a definite chemical compound or not, but is inclined to think it is a result of the splitting up of the complicated molecules of the protoplasm of the egg cells; it is undoubtedly the material from which hæmoglobin is formed. The author believes his experiments prove that food does not contain iron in inorganic combinations, but that it exists only in complex organic compounds which have been formed by the vital processes; it is absorbed and assimilated in this form, and then converted into hæmoglobin. The almost unanimous opinion of physicians as to the efficacy of preparations of iron in chlorosis and their utility in forming hæmoglobin, appears to contradict these conclusions, but the fact remains that inorganic iron is not assimilated. The apparent contradiction may be explained by the hypothesis that inorganic iron salts prevent the decomposition of the organic iron compounds in the intestinal canal.

J. F.

**Effects of Phenylhydrazine on the Organism.** By G. HOPPE-SEYLER (*Zeit. Physiol. Chem.*, **9**, 34—39).—Fischer has investigated the combinations of phenylhydrazine with aldehydes and ketones. Its compounds with the carbohydrates are especially interesting to physiologists; they are soluble with difficulty and easy to isolate. The study of its behaviour in the animal body should therefore throw light on the formation of certain secretions of great importance. The author's experiments in this direction, although not answering his expectations, are interesting.



On five occasions, the substance was administered to rabbits, which were then killed and dissected. A dark brown coloration of the organs was observed, particularly the lungs; the venous cavities were filled with a blackish-brown clot, and the small quantity of still fluid blood coagulated at once on being poured into a glass. When shaken up with water, the solution gave the absorption spectrum of oxyhæmoglobin. The kidneys were much swollen; under the microscope the urinary passages were seen to be filled with blood-corpuscles. All the experiments show that the action in the organism causes a change in the colouring matter of the blood. Blood-corpuscles precipitated by common salt were dissolved in a sufficient quantity of water to allow of easy spectroscopic examination; when a little phenylhydrazine was added, it caused a brown coloration, and the oxyhæmoglobin bands disappeared. The spectrum contained no decided bands, but the green and blue were slightly absorbed.

Some of the blood solution was left over mercury until the spectrum of oxyhæmoglobin disappeared completely, and hæmoglobin alone remained. Phenylhydrazine was then added; at the point of contact a red precipitate formed immediately, and the adjoining part of the solution became reddish-purple. Spectroscopically examined, the bands of hæmochromogen were seen; the colour disappeared after some days. When a few bubbles of air were blown through the fluid, it became brown in the vicinity of the air, and the colour spread downwards, without metahæmoglobin being visibly formed; the spectrum showed only a diffused absorption of the green and blue. Other experiments of a similar character lead the author to conclude that both phenylhydrazine and its hydrochloride cause death when administered in small doses, with appearance of extensive alterations in the blood, and consequent hæmaturia; the poison operates more strongly when injected under the skin than when administered by the stomach; the subcutaneous injection of 0.05 gram killed a fair sized rabbit, whilst 0.5 was required to kill a similar animal when administered by the stomach. The action of phenylhydrazine hydrochloride on the blood in presence of oxygen consists in the formation of a characteristic colouring matter, hitherto unobserved, with sharply defined absorption bands; this passes easily into another substance without a distinctive spectrum. Pure phenylhydrazine operates in a different manner, due to its alkalinity, as it forms hæmochromogen from hæmoglobin in absence of oxygen.

J. F.

**Action of Trichloracetic Acid.** By L. HERMANN (*Pflüger's Archiv*, 35, 35—44).—Soporific properties have been frequently ascribed to this acid by various writers. The author has several times disputed the accuracy of these statements, and now shows that trichloracetic acid is destitute of any trace of hypnotic action, even when injected in very large quantities. Its most characteristic action, when injected in considerable quantity, is the production of paralysis, starting from the hinder extremities.

A. J. G.

**Behaviour of Skatolecarboxylic Acid in the Organism.** By E. SALKOWSKI (*Zeit. Physiol. Chem.*, 9, 23—33).—As shown by the

previous investigations of the author and his brother, this acid is a constant product of putrefying albumin; the possibility therefore exists that it is formed during life in the intestinal canal, either as a physiological or pathological product, and that it may perhaps be present in other organs. Its great resistance to the action of bacteria suggests the idea that it may be reabsorbed and appear in the urine. To decide the question, certain experiments were made. A dilute solution of the acid was introduced into the stomach of a rabbit; about  $1\frac{1}{2}$  hours afterwards the animal passed urine in which distinct reactions of the acid were observed, urine previously passed being free from it; for two days the quantity increased, and then ceased. This shows that the acid passes unaltered through the body. A second experiment gave a similar result; in two other experiments pure skatole was employed; the urine gave the reactions of the acid. The author, in summarising his experiments, thinks the acid forms a regular constituent of urine in cases of peritonitis and inflammation of the ileum, &c., and that when present it can be detected with great ease. J. F.

**Changes in the Chemical Composition of Certain Secretions during Cholera.** By G. POUCHET (*Compt. rend.*, 100, 220—222, and 362—364).—In cases of cholera, the bile collected very shortly after death is colourless and of a gelatinous consistency, and contains a large proportion of water. The greater part of the solid matter consists of albumin and mucin, but leucine, tyrosine, and glucose are always present, together with fat globules, crystals of fatty acids, and cholesterin. The bile also contains products of the decomposition of the bile pigments, which oxidise and reproduce the colour when exposed to the air after removal of the albuminoids.

The vomit frequently contains constituents of the bile.

The alvine ejections are very watery and almost colourless. They contain a relatively large proportion of urea and sodium chloride, especially the latter. The ptomaine described in a former paper (*Compt. rend.*, 99) can be extracted with chloroform, and is a colourless liquid with the characteristic odour of pyridine bases. It oxidises when exposed to the air, becoming first rose-coloured and then brown, is distinctly alkaline, and gives the general reactions of the alkaloids. It instantly and energetically reduces a mixture of potassium ferricyanide and ferric chloride, and it also reduces salts of platinum and gold.

The vapours given off when a solution of the alkaloïd or its hydrochloride is evaporated on a water-bath exert a violent poisonous action, many of the symptoms being those which are characteristic of cholera. The isolated alkaloid, however, is not so violently poisonous, probably owing to the ease with which it undergoes oxidation during the processes necessary for its isolation and purification.

The ejections contain the products of the reduction of bile pigments, but they are almost invariably free from skatole, as Brieger has observed in cases of typhoid fever.

The urine during the period of reaction contains a larger proportion of organic matter, especially urea, and a smaller proportion

of inorganic salts. Sulphates are present in somewhat higher proportion with respect to the amount of urea, but the quantity of sulphur eliminated in the form of sulpho-acid is very small, and in many cases *nil*. The quantity of sodium chloride present is only one-tenth the normal amount, and the proportion of phosphates, especially earthy phosphates, is also diminished. Amongst substances not normally present, the urine contains bile salts in variable quantity, albumin in somewhat large proportion (5—9 grams per litre), glucose, often in very small quantity, and a peculiar albuminoid. The urine contains a very small proportion of a fixed alkaloïd, which does not resemble that extracted from the alvine ejections.

The blood serum contains a relatively large proportion of bile salts, and in one case it gave the chemical and spectroscopic reactions of bile pigments.

It is evident from these results that Asiatic cholera is characterised by extremely energetic processes of reduction. C. H. B.

**Biliary Acids.** By RIETSCH (*J. Pharm.* [5], 11, 158—161).—The paper describes in detail the methods used by the author in testing blood or urine for biliary acids. In these methods there is nothing new; but the purpose of the paper is to state, with some reserve, the negative results obtained in a limited series of experiments on the blood and the urine of cholera patients at a certain stage of the disease. Contrary to results that have been published, the author found no trace of biliary acids, and therefore he is not inclined to regard their presence as a constant characteristic of cholera. R. R.

**Fate of Morphine in the Organism.** By W. ELIASSOR (*Chem. Centr.*, 1884, 70).—Morphine can be detected with certainty in the urine after its administration in large quantities, but with doses up to a few decigrams morphine is not found as such, although an oxidation-product can be detected. Even when the oxidising process in the organism has been reduced by quinine or curara, small quantities of morphine do not pass unchanged into the urine. After large doses of morphine, a not inconsiderable increase in the elimination of ammonia is observable. J. T.

**Poisonous Nature of Sulphurous Acid.** By MASSANORI OGATA (*Chem. Centr.*, 1884, 694—695).—Sulphurous acid under all conditions is a powerful poison, a solution containing only 0·04 per cent. producing, after a few hours, dyspnoea and darkening of the cuticle in all animals. No experiments were made with human beings. The injurious action on the animal organism must be principally sought for in its action on the blood, by which the acid absorbed is converted into sulphuric acid; this latter action does not occur in the case of sulphites.

Dilute blood decolorised with sulphurous anhydride and examined with the spectroscope showed no absorption-bands. Other acids decolorise blood; thus 5 c.c. of diluted blood was decolorised by 0·74 mgrm. HCl, 1·28 mgrm. SO<sub>2</sub>, 1·34 mgrm. H<sub>2</sub>SO<sub>4</sub>, 1·41 mgrm. HNO<sub>3</sub>, and by 4·11 mgrms. acetic acid. H. P. W.

**Action of Potassium and Sodium Salts on the Unstriated Muscles of various Animals.** By O. FLÖEL (*Pflüger's Archiv*, **35**, 157—173).—Corresponding salts of potassium and sodium when used, either solid or in solution, as stimuli to the unstriated muscles of the intestine, &c., show a marked difference in action, the potassium salts causing a more vigorous contraction. The results confirm those obtained by Nothnagel (*Archiv. Anat. Physiol.*, **88** and **89**).

A. J. G.

**Toxicological Contributions.** By E. HESS and B. LUCHSINGER (*Pflüger's Archiv*, **35**, 174—197).—In these experiments, made to ascertain the influence of temperature in accelerating or retarding the action of various poisons, rabbits were poisoned by the subcutaneous injection of chloral hydrate, alcohol, coniine, or salts of mercury, platinum or thallium, and then placed in chambers heated at fixed temperatures. Corresponding experiments were made on animals at the ordinary temperature, and to exclude the possibility of an injurious action of the higher temperature employed, unpoisoned animals were always heated at the same temperatures as those poisoned. The results are thus summarised. Strongly heated, poisoned animals always die sooner than those kept at the ordinary temperature, whilst, on the other hand, moderate heating conduces to the longest continuance of life.

Experiments with animals poisoned with copper or platinum salts show that these poisons largely diminish the oxidising power of the organism; this being shown both by the very great diminution of the amount of carbonic anhydride expired and in the much smaller amount of benzene that could be oxidised to phenol when passed through the system.

A. J. G.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Influence of Culture Fluids and Reagents on the Growth of the *Bacillus Tuberculosis*.** By C. T. WILLIAMS (*Proc. Roy. Soc.*, **36**, 510—512).—The object of this research is to determine the conditions under which the *Bacillus tuberculosis* from the sputum of patients in advanced phthisis grows in various cultivation liquids and antiseptics. As a result, it is shown that the bacillus is characterised by its durability of structure, as evidenced by its not being destroyed by strong acids; it does not multiply in distilled water, but does so largely in beef solutions. Arsenious and boric acids and mercurous chlorides do not interfere with its development, but rather promote it, whilst quinine and iodine appear entirely to arrest its growth and destroy its power of multiplication. V. H. V.

**Bacteria.** By L. BRIEGER (*Zeit. Physiol. Chem.*, **9**, 1—7).—In a previous paper, the author has described the method by which he

obtains pure cultures of bacteria from human fæces; the sample was placed in a sterilised half-litre flask in which water had been long boiled, shaken up so as to be finely divided; 20—30 c.c. of the mixture was then placed in a shallow dish containing 200—300 c.c. of Koch's peptonised gelatin, slightly warmed, the contents mixed by agitation, the dish covered with another of larger size, but inverted, and so closed as to prevent the entrance of bacteria from the air, and the whole arrangement covered with a bell-glass. The arrangement was kept at ordinary chamber temperature; after a short time, micrococci made their appearance in different places, and the species could be isolated. In a previous paper, the author described the bacteria which decompose carbohydrates, and also a coccus which produces ethyl alcohol from both grape- and cane-sugar, but is not dependent on the last two for its existence, as it also lives on albumin, white of egg, serum-albumin, and fibrin; it has not, however, the power of liquefying those substances, nor does it produce any chemical change in them, at any temperature. A bacillus is also described which forms irregular concentric rings on Koch's gelatin, and which, when injected into guinea-pigs, kills them instantaneously; it has not the power of decomposing albumin; it is a remarkable feature of this bacillus, that when left a long time in the nutritive matter its central portions assume a yellowish-white colour caused by an incrustation of salts—no matter whether cultivated on carbohydrates or albumin, at high or low temperatures; when injected into the blood of guinea-pigs, it is injurious, but rabbits and mice are not affected; its action on sterilised grape-sugar at 36—38° produces propionic acid.

Other species of bacteria have been obtained by the author from fæces, but are not described.

Experiments were also made with the coccus which has been described by Friedländer as the excitant of the croupous form of pneumonia; it was cultivated with success in solutions of grape- and cane-sugar neutralised with lime and containing fibrin and nutrient salts, sodium chloride, potassium phosphate, and magnesium sulphate.

The author describes the precautions used in preparing sterilised flasks, &c.; he took the smallest portion of pneumonia cocci on a platinum needle, and introduced it into a flask containing the sterilised nutriment, placed in the incubator at 36—38°, the liquid soon became turbid, but without evolution of gas; after eight hours gas bubbles were slowly disengaged from the bottom of the flask containing the calcium carbonate; after twelve hours the gas passed freely, and the mixture became of a dirty yellow colour and opaque. At 40° gas ceases, but re-commences when the temperature falls. These cultures, even after two months, when injected into the breasts of mice and guinea-pigs, produced distinct pleuritic symptoms; the guinea-pigs resisted the effects strongly, few of them dying; their exudations contained cocci and minute rods in their characteristic capsules. If the original infected solution be distilled with dilute sulphuric acid, the distillate contains principally acetic acid with some formic acid and ethyl alcohol. The author considers that Friedländer's pneumonia coccus has but a very slight power of transformation, and that other factors must enter into consideration when they produce inflammatory

symptoms. Large flat dishes containing peptonised gelatin were infected with streaks of cocci by means of a platinum needle, with the usual precautions. The cocci grew quickly; the centres of the streaks showed the usual yellowish coloration.

Chemically examined, the bacteria gave an alkaline reaction, and their composition was as follows:—

Moisture.....	84.20	per cent.
Dry substance .....	15.80	„
Fat in dry substances .....	1.74	„
Ash in dry substance deprived of fat .....	30.02	„
Nitrogen in dry substance deprived of fat .....	9.50	„

The ash consists of calcium phosphate, magnesium phosphate, and sodium sulphate and chloride.

The organic substance of the coccus is imperfectly soluble in water and cannot be Nencki's mykoprotein, from which it is distinguished by containing less nitrogen. There is nothing in the chemical constitution of the cocci to account for their virulent character. The author tried to produce ptomaines from the pure cultures, but without success.

J. F.

**Observations concerning Organisms which produce Zymases.** By A. BÉCHAMP (*Compt. rend.*, 100, 458—461).—A claim for priority in the discovery of the functions of microbes in digestion, fermentation, &c.

C. H. B.

**Exchange of Gases between Lichens and the Atmosphere.** By G. BONNIER and L. MANGIN (*Chem. Centr.*, 1884, 825—826).—The lichens are generally considered to be plants which, at least with regard to the carbon they assimilate, are quite independent of the substance upon which they grow. The authors endeavoured to ascertain if the amount of carbonic anhydride in the air was sufficient to account for the quantity of assimilated carbon, or whether it was derived from some other source. Those portions of the lichens free from chlorophyll (the hyphens), as well as the parts containing that substance (the gonidia), constantly absorb oxygen and exhale carbonic anhydride, therefore a loss of carbon must take place. But during the day, the chlorophyll substance effects a certain amount of assimilation, and thus carbon is obtained for the whole body. At night a loss of carbon, due to the breathing of all parts takes place, and in day time the same action goes on, but some amount of carbon is also gained. The question is, does the gain exceed the collective loss? The following species were experimented with: *Cladonia rangiferina*, *Evernia prunastri*, *Parmelia caperata*, and *Peltigera canina*. The experiments were conducted in a confined atmosphere. The authors observed, that in the dark, in diffused light, in direct sunlight, and at temperatures from 10—32°, an absorption of oxygen and an evolution of carbonic anhydride took place, even in saturated air, which appeared to be the best for the development of the lichens. *Cladonia*

*rangiferina* exposed to bright sunlight at 30° in a saturated atmosphere, absorbed in two hours 6·75 per cent. of oxygen, and evolved 4·64 per cent. CO<sub>2</sub>. The results in diffused daylight, and at lower temperatures being similar, the action of the chlorophyll does not compensate for the loss of carbon even under the most favourable conditions. Oxygen is absorbed during day and night, and experiments showed that the volume of evolved carbonic anhydride is always smaller than that of the absorbed oxygen.

From these results, it follows that lichens do not derive all their carbon from the air, and it remains to be seen from what sources it is obtained.

H. P. W.

**Formation of Nitrates in Plants.** By BERTHELOT and ANDRÉ (*Ann. Agronom.*, 11, 43—47; from *Compt. rend.*, 98, 1506; 99, 355, 403, 428, 493, 518, 550, 591, 683).—An abstract of the conclusions arrived at by the authors after a very extended series of observations. All plants contain nitrates, and the proportion varies from a trace to 15 per 1000 of dry weight (potato), 28 per 1000 (wheat), and even 150 per 1000 (*amarantus*). The greatest proportion is found in the stem, less in the root, and least in the leaf, where reduction of the nitrate takes place.

A crop of borage contained as much as 120 kilos. saltpetre per hectare. Since nitric nitrogen equivalent only to 4·40 kilos. saltpetre per hectare was contained in the rainfall of 1883, and since the soil contained by careful analysis only 54 kilos. saltpetre per hectare to a depth of 0·325 metre, the authors conclude that nitrates are formed in the plant itself by a nitrifying power supposed to reside in the living cells and to resemble the action of nitrifying ferments in the soil.

J. M. H. M.

*Note by Abstractor.*—The authors, in seeking the source of the nitrates found in the borage crop, do not appear from this Abstract to have taken into consideration the *continuous* formation of nitrates in the soil.—J. M. H. M.

**Acid Amides from the Decomposition of Albumin.** By E. SCHULZE (*Zeit. Physiol. Chem.*, 9, 63—126).—The author refers to the work of Hlasiwetz, Habermann, and Schützenberger in this direction. The present experiments were undertaken on account of the discovery of phenylamidopropionic acid in young lupine plants, and as it was supposed that this had its origin in the decomposition of albumin during germination, it was thought desirable to inquire if it was also a product of the decomposition of other albuminoid materials by means of acids or baryta-water. The presence of the substance has not been noticed by other investigators, but the small proportion in which it is present and the difficulty of its isolation may account for it having been overlooked.

The albuminous substances employed were the kernels of the pumpkin, previously examined by Barbieri and Grüber, and the seeds of lupines, investigated by Ritthausen; the experiments are described at length; their results, whilst agreeing with those of the investigators previously named as to the formation of glucamic



acids, leucine and tyrosine, demonstrate in addition the presence of phenylamidopropionic acid. J. F.

**Proximate Constituents of Hedychium Spicatum.** By J. C. THRESH (*Pharm. J. Trans.* [3], 15, 361—362).—The light petroleum extract of the rhizome of *Hedychium spicatum* deposits crystals of *ethylic methylparacoumarate*,  $C_{10}H_9EtO_3$ , whilst the uncrystallisable portion contains an odorous principle and a fixed oil in addition to a large proportion of this ethereal salt; the mixture on hydrolysis yields, in addition to paracoumaric acid, an acid insoluble in boiling water, but crystallisable from alcohol. The following is the result of the analysis of the rhizome of *H. spicatum*:—

Ethylic methylparacoumarate.....	3.0
Fixed oil, &c. ....	2.9
Acid resin, &c. ....	2.7
Glucoside or saccharine matter .....	1.0
Mucilage.....	2.8
Albuminoids, organic acid, &c. ....	1.9
Starch.....	52.3
Water.....	13.6
Ash.....	4.6
Cellulose, &c.....	15.2

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100.0

D. A. L.

**English Rhubarb.** By W. ELBORNE (*Pharm. J. Trans.* [3], 15, 136—137).—The following results show the percentage of the more important constituents found in the English rhubarb, as compared with the quantities of the same constituents found in the Asiatic drug. I and II *Rheum officinale*, III *R. rhaponticum*, IV East Indian rhubarb.

	I.	II.	III.	IV.
Cathartic acid.....	3.5	3.2	3.3	4.5
Chrysophan and tannic acid	14.3	11.7	12.5	11.7
Resin.....	2.6	2.0	3.4	4.6
Mucilage.....	6.5	4.8	4.1	4.0

In ordinary cultivation (I) the young offsets are planted on an average soil two years after the last manuring; in high cultivation (II) the plants are grown on very rich soils with liberal dressings of manure. The rhaponticum is an ordinary cultivation.

D. A. L.

**Japanese Tea and Tobacco.** By J. TAKAYAMA (*Chem. News*, 50, 299—301).—The Japanese methods of preparing tea and tobacco for the market are described. Various kinds of tea from the Uji district have been analysed and the results are given in tables in the original.

In Japan, *Nicotiana chinensis* and *N. tabacum* are the varieties of the tobacco plant cultivated. It grows from 3 to 5 feet high, bears a rose-coloured flower, and is cultivated in almost every province;

the best leaves are produced in Hizeu, Hitachi, Satsuma, and Nagato. Analyses of these are given. D. A. L.

**Chemistry and Botany of the *Strychnos Nux Vomica* Indigenous to Ceylon.** By W. R. DUNSTAN and F. W. SHORT (*Pharm. J. Trans.* [3], 15, 1—6).—The paper contains a full botanical description of the *Strychnos nux vomica* and other results of the authors' investigations. The conclusions arrived at are that the pulp of the fruit is poisonous, and, in addition to strychnine and brucine, contains the glucoside loganin (comp. this vol., p. 396). The amount of alkaloid in the seeds of *Strychnos nux vomica* varies directly as their size, and inversely as their number in the fruit. The seeds from the Ceylon plant are especially rich in alkaloid, one specimen yielded 5·34 per cent. D. A. L.

**Composition of the Ash of Equisetaceæ, and its Bearing on the Formation of Coal.** By DIEULAFAIT (*Compt. rend.*, 100, 284—286).—The author has examined 168 samples of the ash of various existing species of Equisetaceæ collected in different localities. Although the ashes of different species vary considerably in composition, they are all characterised by the presence of calcium sulphate in large excess, and the total absence of alkaline carbonates. The proportion of ash varied from 5·2 to 8·3 per cent. of the fresh plant, and the mean amounts of potassium sulphate and calcium sulphate in the ashes were 12·0 per cent. and 14·3 per cent. respectively. The mean percentage of sulphuric acid was 13·91, whilst the amount of this acid in the ashes of other plants collected in the same places was not more than 1 per cent. These latter ashes also contained a large proportion of alkaline carbonates.

The presence of such large quantities of sulphuric acid in the Equisetaceæ is obviously one of the causes of the presence of sulphur in coal. C. H. B.

**Continuous Growth of Wheat at Rothamsted during the Twenty Years 1864—1883.** By SIR J. B. LAWES and J. H. GILBERT (*Jour. Roy. Agric. Soc.*, 1884, 391—481; *Ann. Agronom.*, 11, 5—27).—Wheat has now been grown continuously for over 40 years on certain experimental plots at Rothamsted. The discussion of the results obtained during the first 20 years is contained in the *Journal of the Royal Agricultural Society* for 1864; the present very elaborate memoir reports and discusses the results of the second twenty years, 1864—1883 inclusive. The following general conclusions, arrived at after an exhaustive digest of all the available data, are best given in the authors' own words:—

A soil, which in the ordinary course of agriculture would have received an application of manure before another crop was sown, has produced 40 crops of wheat in succession, averaging 14 bushels per acre, solely by means of its existing fertility.

At the commencement of the experiment, the soil contained a large amount of organic nitrogen derived from the *débris* of pre-existing vegetation. It also contained a large amount of the mineral food of plants.

Every year a certain portion of the organic nitrogen has been nitrified by organisms existing in the soil.

Part of the nitrates formed has been employed in the growth of wheat crop; part has been washed out of the soil or otherwise lost.

The loss of nitric acid is greater in wet seasons, and the amount taken up by the wheat crop is in consequence smaller. Dry seasons should, therefore, be favourable for the production of large crops of wheat.

The stock of soil fertility in the form of organic nitrogen has been considerably reduced during the 40 years that the experiments have been carried on, and the amount of such reduction has been ascertained by analyses of the soil made at different periods. The stock of both potash and phosphoric acid has also been largely reduced.

Although so much soil fertility has been removed, the stock that remains would appear to be sufficient to grow crops of wheat for a very long period. The produce, however, must in process of time necessarily be lower than it has hitherto been.

Mineral manures alone have added very slightly to the produce grown upon the unmanured land.

Manures containing nitric acid alone, or some compound of nitrogen which is easily nitrified, have considerably increased the crop.

The soil, therefore, contained a stock of minerals which the wheat crop was unable to make use of, owing to the insufficient supply of nitrogen in some available form.

Manures consisting of potash, phosphoric acid, and ammonia or nitrates appear competent to grow large crops of wheat continuously.

A given weight of nitrogen as nitric acid has produced more growth in the wheat crop than the same weight of nitrogen in salts of ammonia.

The amount of nitrogen supplied in manures is very much in excess of the amount recovered in the increase of the crop.

After a certain amount of growth has been reached each increase of crop requires a proportionately larger application of manure. When the price of grain is high, larger crops can be grown more profitably than when the price is low.

When farmyard dung is employed to grow wheat, a considerably larger amount of nitrogen must be applied to produce a given increase in the crop, as much of the nitrogen contained in the dung is not in an active form.

A given weight of nitrogen in the form of nitric acid will produce more growth in the crop to which it is applied than the same weight of nitrogen in dung, but the influence of the nitrate on succeeding crops will be very much less.

There is no evidence to show whether the whole available effect of the nitrogen in the one manure is greater than it is in the other.

In the absence of vegetation, or when applied to crops in excess of their requirement, both potash and phosphoric acid form insoluble compounds with the soil, and become available for future crops.

In the absence of vegetation, or when the amount supplied is in excess of the requirement of the crop, nitrates and salts of ammonia do not appear to form permanent compounds with the soil, but, on

the contrary, are liable to be washed out by rain, or to be otherwise lost.

The application of a larger amount of nitrogen as nitrates or salts of ammonia than the crop could utilize owing to a want of minerals does not appear to prevent the nitrification of the organic nitrogen of the soil.

The stock of nitrogen of the soil itself, therefore, may be reduced, although the annual application of nitrogen may be much in excess of the amount of that substance removed in the crop.

When large crops of wheat have been grown by the application of nitrates or salts of ammonia with mineral manures, the soil does not appear to have gained or lost fertility. Nitrification of the organic matter of the soil may have gone on as usual, but the loss has been made good by the amount of nitrogen stored up in the stubble and underground roots of the large crops previously grown.

When dung is applied continuously to land, the accumulation of unexhausted fertility becomes very large, and the removal by crops of the substance accumulated would extend over a long series of years.

Dung applied to land in the ordinary processes of agriculture will not be entirely exhausted until many years have elapsed from the time of its first application.

J. M. H. M.

### Chemical Composition of Wheat and Maize as Influenced by Environment. By C. RICHARDSON (*Amer. Chem. J.*, 6, 302—317).

—The author tabulates the results of 407 analyses of wheat grown during the past few years, and analysed in the laboratory of the Washington Agricultural Department. The general results agree with those already published (*Abstr.*, 1884, 1404). American wheats are deficient in albuminoids as compared with those of other countries: they are lighter in weight per 100 grains: they contain less water, about the same percentage of ash, more oil, and a smaller amount of fibre. The deficiency in water is probably due to a drier climate, and the smaller amount of fibre to the hotter summers and shorter period of growth. The lack of albuminoids is not due entirely to enhanced formation of starch, as the weight of 100 grains of American wheat is no greater, in fact somewhat smaller, than that of foreign specimens. The following table shows the variations in the composition of American wheat:—

	Highest p. c.	Lowest p. c.	Average.
Water .....	12·49	7·67	10·16
Ash .....	3·57	0·80	1·92
Oil .....	3·57	1·40	2·16
Carbohydrates .....	78·66	64·84	71·98
Fibre .....	3·05	0·44	1·80
Albuminoids .....	18·03	7·70	12·15
Weight of 100 grains in grams .....	5·924	1·830	3·644

The extreme liability to variation in the albuminoids is in striking contrast with the case of the same constituent in maize, where the variation is only small. The locality has doubtless considerable influence on the quantity of albuminoids present, as a regular grada-

tion of improvement in this respect takes place from east to west. On the Pacific coast, however, the albuminoids are the lowest. The increase of albuminoids, accompanied with increased weight, denotes that the changes are due to the soil, that of the east being more exhausted and not able to furnish such supplies of nitrogenous constituents as the richer ones of the west. The conditions of the environment do not seem, however, in any case to favour, for any length of time, the growth of wheat containing a higher percentage of albuminoids than the average, as experiments with foreign wheats in Colorado have shown; the tendency of these, under the most favourable circumstances of climate, soil, cultivation, &c., is to revert to a constant percentage of about 13 for albuminoids.

About 200 analyses of maize have furnished the basis for the following table:—

	Highest p. c.	Lowest p. c.	Average.
Water.....	15.10	7.40	10.04
Ash.....	3.01	1.03	1.52
Oil .....	7.49	3.92	5.20
Carbohydrates .....	75.73	65.97	70.69
Fibre .....	3.10	0.78	2.09
Albuminoids .....	13.65	7.00	10.46
Weight of 100 kernels in grams .....	53.679	23.605	36.910

The variations in moisture are somewhat larger in maize, but the albuminoids never reach the high percentages at times found in wheat. The longer vegetative period of maize renders it more independent of its environment as far as the composition of the grain is concerned, and the averages for different parts of the country are, therefore, more nearly alike. The size of the kernel of maize does not seem to influence its composition as much as in the case of wheat: the extremes of size are sometimes very wide apart, and in analyses of the largest and smallest kernels selected from 1000 specimens (64.102 grams and 13.858 grams per 100 kernels) the average percentage of albuminoids was found to be 9.09 and 10.50 respectively.

J. K. C.

**First Grass and Aftermath.** By A. RÜFIN (*Bied. Centr.*, 1885, 68).—The first cut of grass or green fodder is vastly superior to the aftermath for dairy cattle.

E. W. P.

**Influence of the Position of the Set on the Potato Crop.** By E. WOLLNY (*Bied. Centr.*, 1885, 24—30).—As there seemed to be a difference of opinion between Kühn and Gülich as to whether the end having most eyes should be set upwards or downwards, Wollny undertook to ascertain the truth with various kinds of potatoes. The results observed in 1874 are by no means conclusive, for in some cases those with the eyes upwards gave the highest yield, in others the contrary was the case. Accordingly in 1876 and 1884 other experiments were made on light humous land, and then some sets were placed shallow, others deep in. Again, however, the results were not very satisfactory, but the conclusions which have been drawn are that on dry soils the position of the set is of importance, whether set deep or

shallow ; in soils holding moisture, the position of the set is not of much importance. Another question investigated was the position of the set when the original tuber had been cut in half. Experiments showed that as a rule the highest yield was obtained when the cut surface was downwards, the probable reason for this being that when the surface lies upwards, the interior of the potato, that is the nourishment for the young plant, is rotted away.

E. W. P.

**Cultivation of Potatoes.** By O. CIMBAL and others (*Bied. Centr.*, 1885, 35—51).—The experiments were on the same principle as those conducted in 1883 (*Abstr.*, 1884, 483), and the results were very similar. The article consists very largely of tables, showing yield and quality of numerous varieties of tubers. Staudacher raised potatoes from the seed of five various sorts, but none of the new potatoes at all resembled the originals from which the seed was taken. According to C. Boursier, potash manure has no influence for good on potatoes, but potassium chloride is less harmful than the nitrate. A few remarks on Jensen's method for the prevention of potato disease are added.

E. W. P.

**Peculiarities and Cultivation of Beet Seed.** By F. KNAUER and others (*Bied. Centr.*, 1885, 15—24).—The mean weight of sugar-beet seed is 185·34 grams per litre. To determine the germination of a sample, Breuer's germinator was found to be the most accurate. This apparatus consists of a rectangular zinc box whose sides are somewhat sloped, the bottom is 10 cm. square, and the height of the walls is 20 cm. It is filled with white sand moistened with rain-water. Soaking in water, rubbing with the hand, and heating to 50° raises the coefficient of germination. The best results are obtained when the seeds are previously heated at 40—45° in moist air, but whether they are exposed to light or not seems to make no difference. Dilute hydrochloric and sulphuric acids aid germination, but nitric acid has no effect ; sodium hydroxide, nitrate, and sulphate are harmful, but sodium chloride is neutral, whilst alum (11 per cent.) assists germination. Briem has treated seeds with water, and evaporated the filtrate, the residue amounting to 6·76—8·71 per cent. of the whole. This residue was brown and very hygroscopic, and when ignited swelled up and "left 55·8 per cent. of organic (?) matter." The percentage of ash varies from 7·5—10·5. The following is the composition of the dried seeds :—

Water .....	11·416	N <sub>2</sub> O <sub>5</sub> .....	0·009
Silica, &c. ....	0·845	NH <sub>3</sub> .....	0·108
P <sub>2</sub> O <sub>5</sub> .....	0·815	Nitrogenous matters .	8·406
SO <sub>3</sub> .....	0·280	Fat and colouring mat-	
Cl .....	0·167	ters .....	5·010
K <sub>2</sub> O .....	1·268	Starch, dextrin .....	17·420
Na <sub>2</sub> O .....	0·657	Cellulose .....	24·600
CaO .....	1·315	Soluble protein .....	4·211
MgO .....	0·947	Undetermined .....	25·526
			<hr/>
			100·000

In 1883 seed, Knauer found impurities, amounting to 1·3 per cent., whilst Märcker found 2·9, and Nobbe 0·56—6·27. Moisture also varies: Nobbe found 13·3 per cent., and Knauer 10·8—12·62. Seeds soaked in water contain 129—140 per cent. of moisture. The small agglomerations of seed absorb more water than the larger; but part of the agglomeration which is not true seed has been termed "ballast," and this on the average amounts to 73·57 per cent. of the whole.

E. W. P.

**Phosphoric Acid in the Soil.** By P. DE GASPARIN (*Bied. Centr.*, 1885, 7—8).

**Influence of Cultivation on the Moisture in the Soil.** By A. HENSCH (*Bied. Centr.*, 1885, 4—7).—The fertility of a soil is largely dependent on the moisture present, and it appears that the quantity which is most advantageous for the crop is 40 per cent. of the total quantity which the soil can retain, but this percentage is dependent on the weather, lay of the land, chemical composition, and physical condition. As capillarity is a very important factor, and as this is capable of alteration, it follows that the amount of moisture present is dependent on the treatment the land receives. An open soil with rough surface, such as is produced by ploughing, &c., will take up more rain than when the surface is comparatively level and unworked, and since the character of the surface is affected by the amount and violence of the rainfall, the consequence is that at first the absorption of water is most energetic, so that the open condition of the soil must be maintained if the requisite quantity of water is to be retained. Humous soils retain nearly double their own weight of water, whilst sandy soils only retain 30—40 per cent. Humous soils lose water more rapidly by evaporation than sandy soils, whilst clay soils hold an intermediate position. As a rule, water evaporates most rapidly from wet soils and when the bottom water is near the surface, but from two soils holding the same quantity of moisture the rapidity of evaporation is dependent on the character of the surface, rough surfaces drying more rapidly than smooth; thus soil rolled by a ring roller dries more rapidly than that rolled by a smooth roller.

E. W. P.

**Use of Potassium Chloride in Agriculture.** By D. ZOLLA (*Ann. Agronom.*, 11, 34—40).—The author has made some experiments tending to show that potassium compounds produce increase of certain crops even on soils well supplied with potash.

*Oats.*—A field of 50 hectares was divided into 17 plots, and sown with grey and black oats (Bernay). Seven of the plots were unmanured, and yielded an average of 2700 kilos. straw and 47·4 hectolitres grain per hectare. Four plots received 45 kilos. potassium chloride per hectare, and yielded an average of 3000 kilos. straw and 47·8 hectolitres grain. Five plots received 190 kilos. potassium chloride per hectare, and yielded an average of 3180 kilos. straw and 51·45 hectolitres grain. All the plots dressed with the potassium salt received it mixed with 300 kilos. gypsum per acre. The soil contained by analysis 0·073—0·292 per cent.  $K_2O$ .

*Lucerne*.—A field of 70 hectares carrying lucerne in its third year had been dressed in February with a manure containing 6 per cent.  $P_2O_5$ , 14 per cent.  $K_2O$ , 3 per cent.  $Na_2O$ , and 20 per cent.  $CaO$ . Alternate ridges received in addition 230 kilos. potassium chloride per hectare. This application produced an immediate beneficial effect on the appearance of the plant, and raised the yield from 915 baskets (of 5 kilos. each) per unmanured ridge to 1078 baskets per ridge of those dressed with the potassium salt. (The author does not state if the potassium chloride was mixed with gypsum in this case also.) The soil contained 0.160 per cent. of potash.

J. M. H. M.

*Note by Abstractor*.—The conclusions drawn by the author appear to be open to much doubt in consequence of this fact. The yields of the individual plots, too, are not stated.—J. M. H. M.

**Manurial Value of Tobacco Stems.** By C. A. GOESSMANN (*Bied. Centr.*, 1885, 67).

		(1.) Connecticut Valley tobacco.	(2.) Havanna.
In 100 parts:	Moisture.....	8.95	11.05
	Ash.....	13.91	13.30
	Nitrogen.....	2.69	2.91
	Potash.....	6.21	3.76
In dry mat- ter.	Soda.....	0.68	0.20
	Lime.....	4.76	4.15
	Magnesia.....	1.14	1.53
	Phosphoric acid..	0.87	0.50
	Ferric oxide ....	?	0.16

From this the author calculates 1000 kilos. to be worth (1) 67.2 and (2) 60.0 marks. E. W. P.

**Manuring Turnips.** By B. DYER (*Bied. Centr.*, 1885, 30—34, from the *Jour. Roy. Agr. Soc. Eng.*, 20, 113—126).—The experiments were conducted in 1882 and 1883 near Horsham, on heavy loam containing  $K_2O$  0.482 per cent.,  $P_2O_5$  0.212,  $CaO$  0.672, and  $SO_3$  0.147. The plots were one-sixth of an acre, and received equal money values of dissolved and undissolved Cambridge coprolites, with and without sheep manure. Plots were also manured with sheep manure alone. In the first year, it was found that the artificial manures brought a larger crop than the dung alone, that the two kinds of artificial manures alone were as good as when combined with the dung, and also that the undissolved was better than the dissolved phosphate. This probably arose from the deficiency of lime in the soil. In the next season, oats were sown, but as the duplicate plots differed so much from the originals, no fair conclusions can be drawn, but it may be remarked that the raw phosphate was superior to the dissolved. To estimate if possible the advantage of the addition of lime to this soil, a further set of experiments was made on some of the land which had received no manure since 1880. This was limed, and then roots again grown with the same manures as in the previous case. Now it was observed



that the manure (cow and horse) yielded best, but the duplicate was very different in its yield to the original, so that if the lower yield be accepted as correct, then the verdict in favour of the farmyard manure must be reversed; also it was noticed that superphosphate was better than undissolved phosphate, proving the advantage of superphosphates on well-limed land, and of undissolved phosphates for land poor in this constituent.

E. W. P.

**Correct Time for the Honey Harvest.** By K. ZWILLING (*Bied. Centr.*, 1885, 67).—Two periods have been chosen in which to remove honey from hives; the first is when the cells are full and unsealed, when the honey is thin; the other period is when the honey has thickened and the cells are sealed. The latter is the correct time to harvest, for then there is enough sugar and formic acid present, which last acts as an antiseptic.

E. W. P.

**Removal of Mildew in Vines.** By P. PICHARD (*Ann. Agronom.*, 11, 27—33).—The vine mildew (*Peronospora viticola*) having caused great damage amongst the vineyards of Vaucluse towards the end of last summer, the author took the opportunity of instituting exact experiments with certain substances recommended as mildew specifics. These substances are all best applied in the liquid form by means of Riley's "atomiser" or spray producer. *Phenol*.—A 1 per cent. solution has no effect; the addition of 0.1—0.5 per cent. glycerol is no improvement. *Phenol and Potash*.—A 1 per cent. solution of phenol with 0.2 per cent. potassium hydroxide exercises a slight effect on the mould; this effect is not increased by the addition of glycerol, and is probably due to the potash alone. *Ferrous Sulphate*.—Solutions of the crystallised sulphate of over 0.2 per cent. strength, blacken the leaves and cause them to curl at the edges, and in time to fall off. Solutions of 0.1—0.2 per cent. strength do not injure the leaves, but arrest the development of the mycelium, the spores, however, remaining apparently intact. *Ferric Sulphate*.—Solutions of 1 per cent. strength slightly injure the leaves. Weaker solutions destroy the mycelium without injury to the leaves, but the strength should not fall below 0.5 per cent. *Alkaline Polysulphides*.—The author considers these to be the most convenient vehicles for sulphuring the vines. He recommends potassium polysulphides, as the potash when washed down into the soil has a manurial value. Solutions of 1—5 per cent. injure the leaves, but a solution of 0.5 per cent. strength may be used without danger, and will destroy the mould. A thin pellicle of precipitated sulphur adheres to the leaf and prevents the reappearance of the fungus.

J. M. H. M.

## Analytical Chemistry.

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**Analytical Operations and Apparatus.** By R. WOLLNY (*Zeit. Anal. Chem.*, **25**, 47—56).

**Estimation of the Halogens in Organic Compounds.** By C. ZULKOWSKY and C. LEPÉZ (*Monatsh. Chem.*, **5**, 537—558).—This method is based on the combustion of organic substances in a stream of oxygen, the combustion being aided by heated platinum (Kopfer, this Journal, 1876, 660). Under these circumstances, iodine is obtained entirely in the free state, bromine mainly in the free state, but to the extent of 1—5 per cent. as hydrobromic acid, and chlorine is obtained partly free and partly as hydrochloric acid. The solution employed for absorption is a mixture of ammonia and hydrogen peroxide, by which the free halogen is converted into the ammonium haloid salt, whilst oxygen is evolved, the reaction in the case of iodine being represented by the equation  $I_2 + H_2O_2 + 2NH_3 = 2NH_4I + O_2$ ; the whole of the halogen is obtained as its ammonium salt, and can be estimated in the usual manner. The most convenient form of platinum for the process was found to be obtained as follows:—Pure quartzite is heated strongly and thrown into water, then ground in an iron mortar till reduced to fragments about the size of hemp-seed, sifted to remove dust and larger particles, and digested with hydrochloric acid to remove iron. 100 parts of the quartzite are just covered with an alcoholic solution of *pure* platinic chloride containing 5 parts of platinum, the whole evaporated to dryness on a water-bath, placed in a glass tube, and ignited in a current of hydrogen. The purity of the platinic chloride is essential, commercial platinum or platinic chloride containing sufficient iron and copper to vitiate the results. The combustion-tube employed is from 50—67 cm. long, and is drawn off and bent sharply downwards at one end; next to the drawn-off end is placed a loose plug of asbestos, then a layer of platinised quartzite of 23—36 cm. in length, held in its place by a short roll of platinum foil. The substance to be analysed is introduced into the tube in a boat or thin tube; finally, the open end of the tube is connected with a reservoir of oxygen. For the analysis of very volatile liquids, an ingenious device is described; the current of oxygen is split, a gentle stream passing through a bulb-tube in which the liquid is placed, whilst the greater part of the oxygen is carried directly to the combustion-tube and there mixes with the vapour of the volatile liquid carried over from the bulb; perfect combustion is thus insured. The drawn-out end of the combustion-tube is attached to a flask containing the absorbing liquid, and immersed in cold water to prevent the decomposition of the hydrogen peroxide by heat. To the flask is further attached a Peligot's tube containing a small quantity of the absorbing liquid; the escaping gases being finally passed through a tube containing cotton wool, moistened with the absorbent, thus ensuring the retention of every trace of halogen. Chlorine com-

pounds require a longer tube for combustion than do substances containing bromine or iodine. As the whole of the iodine is obtained in the free state, it can be absorbed by a solution of potassium iodide and titrated with sodium thiosulphate. A considerable number of analyses of halogen-compounds are quoted, showing that very accurate results are obtained by the method. As hydrogen peroxide frequently contains small quantities of chlorine, it is necessary, if present, to determine the amount and make allowance for it.

Magnesia can with advantage be substituted for lime in the ordinary ignition method of determining halogens.

Sulphur in organic compounds can also be estimated by combustion in the apparatus above described; the liquid used in the absorbing apparatus is either hydrogen peroxide and ammonia, or a strong alkaline solution of potassium hypobromite. The sulphuric acid formed is estimated gravimetrically. The reagents employed must be examined for sulphates.

A. J. G.

**Iodic Acid as an Indicator.** By F. E. FURRY (*Amer. Chem. J.*, 6, 341—345).—A mixture of an iodide and iodate in solution has been suggested as an indicator for the presence of free acid, the amount of iodine liberated showing the quantity of free acid present. It has been noticed that the blue colour with starch, after being discharged by hyposulphite, generally reappears after a few minutes, and this fact has been ascribed to the atmospheric carbonic anhydride. The author has undertaken a series of experiments to ascertain the accuracy of this assumption, and whether any other conditions interfere with the value of this indicator.

A dilute standard solution of sulphuric acid was employed, and the extreme delicacy of the end-point noted, 0.08 mgrm.  $\text{H}_2\text{SO}_4$  in 100 c.c. water being sufficient to yield a blue colour with the indicator. The influence of dilution on the test was next observed, the results showing that as the dilution increases the liberation of iodine is less, and the blue colour on its reappearance requires more hyposulphite for its discharge. The phenomenon of after-coloration may be therefore ascribed almost wholly to the action of a residual quantity of sulphuric acid, and only in slight degree to atmospheric carbonic anhydride.

Hydrochloric, nitric, salicylic, and picric acids act also in precisely the same way as sulphuric acid. With other acids, however, such as boric, citric, tartaric, oxalic, acetic, and benzoic acid, satisfactory results were not obtained in any state of dilution: after long periods of time the full equivalents of iodine were never liberated.

In the presence of neutral salts of the alkalis with the strong mineral acids, the indicator may be safely used: in saturated solutions only is there a slight interference. Salts of the organic acids, on the contrary, and borates, even when present in small amount, render the method uncertain.

J. K. C.

**Estimation of Oxygen in Air.** By W. HEMPEL (*Ber.*, 18, 267—282).—The author points out the importance of having exact determinations of the composition of the atmosphere for comparison by future generations. The analyses should be accompanied by meteorological observations.

logical observations, as rain, pressure, temperature, &c., produce certain changes in composition. The apparatus employed for estimating the oxygen is too complicated to describe without diagrams; the measurements are made at a constant volume and temperature, but at varying pressure. The method is accurate to 0.02 per cent. At the end of the paper a number of determinations are recorded together with meteorological observations which were made at the time and place from which the air examined was taken.

A. K. M.

**Determination of Nitrogen by the Copper Oxide Method.**

By C. W. DABNEY and B. v. HERFF (*Amer. Chem. J.*, 6, 234—241).—A comparison of results obtained by Ruffe's method (*Trans.*, 1881, 87), and the copper oxide method as modified by Johnson (*Amer. Chem. J.*, 2, 27); the apparatus used in the latter method is fully described. Both methods give equally good results. H. B.

**Modification of Zulkowsky's Azotimeter.** By A. GAWALOVSKI (*Zeit. Anal. Chem.*, 24, 61—63).

**Detection of Nitrous and Nitric Acids.** By R. WARINGTON (*Chem. News*, 51, 39—41).—In the present communication the author gives the results of experiments on the various tests for nitrous and nitric acid. The delicacy of a test depends greatly on the manner in which it is applied, therefore old as well as new tests are included in the present note. In nearly all cases blank experiments were made under exactly similar conditions to those of the test experiment.

*Detection of Nitrous Acid. Iodide Test.*—1 c.c. of Trommsdorf's reagent is added to 5 c.c. of nitrite solution, and the mixture acidulated with one drop of dilute sulphuric acid (1 in 5); under these conditions a solution containing 1 part of nitrous nitrogen per million of water soon caused an abundant liberation of iodine, whilst 1 in 20 millions gave rise to a blue coloration in 3 minutes, and solutions containing 1 in 100, and 1 in 200 millions, gave a blue tinge in 30 and 60 minutes respectively. The blank experiment only began to colour in 4 hours. The *metaphenylenediamine* test is accelerated by warming. Four drops of a solution containing 5 grams per litre, and one drop of dilute sulphuric acid added to 5 c.c. of nitrite solution, causes a speedy and very distinct reaction with one part of nitrous nitrogen per million of water, but with 1 in 10 millions the change begins in 2 minutes, and the final colour is only pale straw-yellow. *Paramidobenzene-azo-diamethylaniline* test (Meldola, *Trans.*, 1884, 108).—A solution containing 0.16 gram of this reagent per litre is employed, and one drop of test solution, one drop of dilute sulphuric acid, and finally a slight excess of ammonia, are added to 5 c.c. of nitrite solution. No reaction is obtained with solutions containing 1 part nitrous nitrogen per million of water, when the reagents are added immediately after one another, but when the solution acidified with sulphuric acid is heated for 2 minutes in boiling water, then on addition of the ammonia a distinct blue coloration is obtained even with 1 part of nitrous nitrogen in 10 millions of water, and a pale

sap-green with 1 in 100 millions. The colour is somewhat fugitive. With the *naphthylamine test*, using one drop of saturated solution of sulphanilic acid, one drop of dilute hydrochloric acid, and one drop of saturated solution of naphthylamine hydrochloride, as already stated (Trans., 1881, 229), 1 part of nitrous nitrogen in 100 millions gives a reaction in six minutes, 1 in 500 millions in an hour or two, whilst even 1 in 1,000 millions can be detected.

*Detection of Nitrous and Nitric Acids.*—The four following tests give a reaction with both nitrous and nitric acid, but the reaction of the first mentioned is the only one which is characteristic for these substances, inasmuch as the other three give the same reaction with all oxidising agents. The *ferrous sulphate test* is equally sensitive with both nitrous and nitric nitrogen, and is conducted most effectually in the following manner. Place 1 c.c. of nitrite or nitrate solution into a tube, and pour down 2 c.c. of concentrated sulphuric acid so as to form a lower layer, mix suddenly, and run in immediately 3 c.c. of a cold saturated ferrous sulphate solution, which forms an upper layer. In this way, with solutions containing 1 part of nitrous or nitric nitrogen in 100,000 parts of water, the coloured band appears at once, with 1 in 200,000 there is a faint reaction in 1 or 2 minutes, whilst with 1 in 300,000 the reaction is very slight. *Indigo test* (according to Boussingault).—The concentrated substance is boiled with a few drops of indigo, and successive quantities of strong pure hydrochloric acid, the disappearance or discolouring of the indigo is the indication of oxidation. One division of Boussingault's weakest indigo = 0.00077 milligram of nitric nitrogen. This test does not answer in the presence of many organic substances. *Brucine test.*—To get a distinct pink colour, 5 c.c. of concentrated sulphuric acid are added gradually to a cooled mixture of 2 c.c. of the liquid and one drop of brucine sulphate. One part of nitric nitrogen in 10 millions of water soon gives a reaction, whilst 1 in 20 millions causes a faint tinge after some time. With nitrous nitrogen, 1 part in 1 million of water gives a full pink, but 1 in 10 millions produces scarcely any reaction. *Diphenylamine test.*—The reaction is assisted by heat, by adding a large excess of sulphuric acid, also by the presence of chlorides, but only when the volume of sulphuric acid is not greater than that of the liquid taken. The colour is fairly permanent, and increases on standing. With 2 c.c. of liquid, two drops of diphenylamine solution and 5 c.c. concentrated sulphuric acid, 1 part of nitric nitrogen in 1 million of water produces a deep blue at once, 1 in 10 millions a pale blue after a few minutes, whilst 1 in 20 millions gives no distinct blue. (Trans., 1884, 644, it is stated that solutions of this strength do give the reaction; it has, however, since been observed that the reactions obtained in those experiments were due to an added impurity.) Nitrites act in a similar manner, but more rapidly. One millionth part of a gram of nitric nitrogen can be detected by this test when using 1 c.c. of liquid.

*Detection of Nitric Acid in the Presence of Nitrous Acid.*—There is no satisfactory method for effecting this when the quantity of nitric acid is very small, for nitric acid is either produced, as in the second and third, or only vaguely indicated, as in the first of the following

methods. 1st. Estimate the total nitrous and nitric nitrogen as ammonia or nitric oxide; and then the nitrous nitrogen with permanganate, or with phenylenediamine, the difference between the two estimations, is due to nitric nitrogen. 2nd. Piccini recommends destroying nitrites by boiling acidified solutions with carbamide, and then testing for nitric acid. 3rd. Muir suggests conversion into ammonium salts, and evaporating to dryness to destroy nitrite.

D. A. L.

**Volumetric Estimation of Nitric Acid.** By A. LONGI (*Zeit. Anal. Chem.*, **24**, 23—26).—This method is based on the fact that stannous salts destroy the blue colour produced by diphenylamine in solutions of nitric acid (comp. Abstr., 1884, 366). The author has found that the accuracy of his method depends on the amount of sulphuric acid present. The titration is effected by a decinormal solution of potassium stannous sulphate, a single drop of diphenylamine solution being added as indicator. Numerous experiments show that the method is quite accurate when 3.5 volumes of concentrated sulphuric acid are present to each vol. of the solution to be tested. It cannot be applied, however, if ferric salts are present in large quantities; concentrated solutions of nitrates should be diluted with water before adding the concentrated sulphuric acid, and, in all cases, the mixture should be cooled before adding the diphenylamine solution.

S. R.

**Recognition of Nitric Acid Stains on Textures.** By H. FLECK (*Chem. Centr.*, 1884, **38**, 716).—The stained cloth is extracted with hot water, and the liquid evaporated to dryness and tested with brucine. If, however, the stains have already been washed with water, they must be cut out and heated with a 20 per cent. solution of caustic potash. Xanthoproteate of potassium is formed, and colours the solution deep orange; on diluting with 10 times its volume of water, filtering, and neutralising with sulphuric acid, yellow flakes separate; these are collected on a filter, and treated with ammonia, when a deep orange-red colour is produced. These flakes cannot be mistaken for those produced by picric or styphnic acids, since both these acids are soluble in boiling water. A control experiment should be made with a piece of woollen rag, previously steeped for 24 hours in nitric acid.

H. P. W.

**Separation of Zinc in Ores.** By T. B. OSBORNE (*Amer. Chem. J.*, **6**, 151—152).—Brunner's method (*Dingl. polyt. J.*, **150**, 369) with the modification described in the next abstract, may be used in the separation of zinc from iron.

P. P. B.

**Separation of Zinc and Nickel.** By T. B. OSBORNE (*Amer. Chem. J.*, **6**, 149—151).—The author's experiments led him to conclude that, in separating these metals by Brunner's method, the best results can be obtained by adding to the solution (diluted to 300 c.c.) enough sodium carbonate to produce a permanent but slight precipi-

tate, then 1 c.c. of hydrochloric acid (sp. gr. 1.1), and, during the precipitation of the zinc by sulphuretted hydrogen, gradually adding 50 c.c. of a solution of sodium acetate, containing sufficient of this substance to react with about one-half the acid set free.

P. P. B.

**New Blowpipe Reagent.** By WHEELER and LUDEKING (*Chem. News*, 51, 88).—The substance to be tested, supported on a slab of plaster of Paris if it forms a coloured iodide, or on charcoal if the iodide is white, is moistened with a saturated alcoholic solution of iodine, and heated in the outer blowpipe flame; the iodide volatilises, and is deposited on the cool parts of the support, where its characteristics and identity can be recognised. In this manner, tin can be detected in the presence of zinc, whilst bismuth gives a brown deposit which is changed to red by the action of ammonia; the molybdenum reaction, an ultramarine-blue deposit, is very striking and distinctive.

D. A. L.

**Lead Assaying in the Wet Way.** By C. ROESSLER (*Zeit. Anal. Chem.*, 24, 1—23).—Storer has shown (*Chem. News*, 1870, 17) that galena in the presence of zinc and hydrochloric acid yields hydrogen sulphide and a spongy mass of metallic lead. The lead being in a porous condition, rapidly oxidises when exposed to the air, and therefore has to be dried in an atmosphere of coal-gas. Good results are obtained by this method with pure galena, but with ores and mining products containing lead the analyses are unsatisfactory. The modification proposed depends on the solution of the spongy lead in a known weight of Wood's metal, the analysis being effected as follows:—The sample is treated with about 30 times its weight of hydrochloric acid of sp. gr. 1.10. If a carbonate is present a corresponding increase in the amount of acid is necessary. The mixture is heated as long as there is any action, and then diluted with an equal volume of water. When sulphuretted hydrogen can no longer be detected, a small stick of zinc weighing about 1 gram is added, and the whole heated on a water-bath to 70°. All the lead is precipitated when a piece of magnesium ribbon dissolves without leaving any particles of lead floating in the solution. The spongy mass is stirred with a glass rod until hydrogen ceases to be evolved, so as to ensure that no zinc remains undissolved. The lead is washed with water, and calcium carbonate is added until the solution is only faintly acid. The weighed quantity of fusible metal is then added to the lead, and when molten, poured into a beaker of cold water, dried and weighed. At least one part of Wood's metal must be employed for each part of lead present. If copper pyrites or other sulphide not decomposed by hydrochloric acid is present, the weighed sample is treated with a few c.c. of aqua regia, and the lead precipitated as sulphate by the addition of sulphuric acid. The precipitated sulphate is filtered, dissolved in hydrochloric acid, and the process then applied. When antimony is present, the two are precipitated as sulphides, and separated by sodium sulphhydrate in the usual way. Another method, used with some success, consists in evaporating the chlorides to dryness, and distilling at 230°, when all the antimonious chloride

is removed from the lead chloride, which can then be dealt with in the way already described. S. R.

**Improvement in the Apparatus used for Precipitating Copper by Electrolysis.** By H. C. FOOTE (*Amer. Chem. J.*, 6, 333—336).—The object of this improvement is to ensure a current of proper strength, and to keep it so for two or three days without changing the battery fluids.

The platinum dishes are arranged on a board, under which the current from the battery passes, and traverses a set of resistance coils and connecting wires. The current first enters a switch under the board, from which it can pass to another switch by three routes, traversing different resistance coils; the same contrivance is then repeated, the current being made to pass further through one, two, or three resistance coils on its way to the platinum dishes, another switch, after the current has attained its required strength, regulating its admission to the required number of dishes. By manipulating the switch handles the current can be made to work uniformly, and in case a dish is removed from the circuit, an automatic arrangement is employed to preserve the uniformity of the current. A coil equal in resistance to the solution in the dish is connected with the latter in such a manner that when the dish is removed the current is made to pass through the coil, and thus the current remains the same in the other dishes. The strength of the current may be ascertained by passing it through acidulated water in an inverted graduated tube, and noting the amount of mixed gases liberated in one minute.

J. K. C.

**Separation of Metals Precipitated by Hydrochloric Acid.** By J. BARNES (*Chem. News*, 51, 97).—Quantitative experiments show that ammonia does not completely dissolve silver chloride when it is precipitated along with mercurous chloride, and in fact, that if the latter greatly predominates scarcely a trace of the silver salt is dissolved by the ammonia.

D. A. L.

**Electrolytic Estimations.** By A. CLASSEN (*Ber.*, 18, 168—171).—A reply to Wieland.

**Estimation of Manganese and Phosphorus in Iron and Steel.** By M. TROILIUS (*Chem. Centr.*, 1884, 717—719).—For analysis 0.5 gram of steel or iron borings, 0.5 gram of specular iron, and 0.2 gram of ferromanganese are sufficient quantities.

*Estimation of Manganese.*—The steel or iron is dissolved in hydrochloric acid, the solution evaporated nearly to dryness, nitric acid added, and the liquid evaporated to 100 c.c. Crystals of potassium chlorate are cautiously added until yellow fumes cease to be given off, more being added as soon as the manganese precipitates, and the solution kept boiling for a short time; cold concentrated nitric acid is then added, the precipitate collected on asbestos contained in a glass tube, washed twice with strong acid, and four times with cold water. Instead of adding cold acid previous to filtering, the solution can be allowed to cool; in either case the formation of potassium permanganate is prevented.



In the analysis of specular iron and ferromanganese, it is not sufficient to treat once with potassium chlorate, but this operation must be repeated several times, with addition of nitric acid. The addition of ferric nitrate facilitates the precipitation.

The precipitate is treated with 100 c.c. of a standard solution of ferrous sulphate in dilute sulphuric acid. As soon as the precipitate has dissolved, the unoxidised iron is estimated, and the manganese calculated from the difference.

Lead, copper, nickel, cobalt, &c., when present, are precipitated with the manganese dioxide, and oxidise the iron sulphate; sometimes on addition of the latter, a characteristic red coloration—due to cobalt—is produced. In one case where the coloration was intense, the author estimated the cobalt, of which there was only 0.03 per cent. The results are accurate.

*Estimation of Phosphorus.*—5 grams of borings are dissolved in nitric acid, the solution evaporated nearly to dryness, and strong hydrochloric acid added, the evaporation is continued, and the dry mass redissolved in hydrochloric acid, hot water added, and the silica filtered off. 20 c.c. strong nitric acid, 80 c.c. molybdenum solution, and 20 c.c. strong ammonia are added to the filtrate, and the whole well shaken until the iron precipitate has dissolved, and then it is allowed to stand 24 hours at 40°. The clear liquid is poured off, and the precipitate collected on a filter, washed and dissolved in warm dilute ammonia, 2.5 c.c. strong hydrochloric acid are then added along with 10 c.c. of magnesia mixture, and the whole well shaken until a distinct precipitate is observable; after adding 5 c.c. more ammonia, and allowing to stand for 12 hours, the precipitate is filtered off, and the phosphorus determined as magnesium pyrophosphate.

H. P. W.

**Ash Determinations.** By JAY (*Bull. Soc. Chim.*, **42**, 218—219).—In order to quickly obtain a white ash without loss of alkaline salts, particularly in the case of wine and of vegetables, the author first evaporates and dries at 100° and then carbonises the residue. A few drops of water are added which disintegrate the carbonaceous mass, and partially dissolve the alkaline salts. The mixture is now evaporated at 100° and dried at 115°. After this the product is ignited in the ordinary way.

W. R. D.

**Titration with Potassium Permanganate Solutions.** By W. LENZ (*Zeit. Anal. Chem.*, **24**, 34—41).—Permanganate solution when used for estimating organic substances in water is untrustworthy, since only those bodies which are very easily oxidised are completely converted into carbonic anhydride.

With grape-sugar, great discrepancies were noticed; the greater the excess of permanganate, the greater the amount used. In no case, however, was the theoretical quantity of permanganate reduced, although about five times the calculated quantity was added. The experiments were repeated by varying the amount of grape-sugar added to a constant quantity of permanganate solution, and then boiling for 10 minutes, but with similar discordant results. With

glycerol, the experiments yielded results still farther from the truth. The permanganate process is therefore useless for either absolute or relative estimations of organic matter.

The oxalic acid solutions used for titrating permanganate should be freshly prepared, as the author finds that centinormal acid loses 15 per cent. of its strength in one week when exposed to diffused daylight. Normal solutions will keep in the dark, if stored in full bottles. Centinormal solutions, even in the dark, lose strength after keeping for a few weeks. The addition of 10 grams of boric acid per litre prevents the decomposition of the oxalic acid, and does not injure its value for titrating purposes. It is best, therefore, to keep decinormal acid containing 1 per cent. of boric acid and dilute it as required. S. R.

**Adulteration of Petroleum by Means of Solar Oil.** By G. HEPPE (*Chem. Centr.*, 1884, 70).—Dry copper butyrate dissolves both in petroleum and in solar oil on warming slightly, giving a bluish-green colour; on further heating the solar oil solution becomes yellow at 120°, and a yellow flocculent precipitate forms, whilst the solution in petroleum remains green and clear, even at 210°. A mixture of the two oils, heated to 120° with the butyrate, gives a yellow flocculent precipitate, or if only a little solar oil be present, a greenish-yellow colour is produced, whilst at 210° the colour becomes pure yellow. On cooling the petroleum solution, the butyrate separates out almost entirely, and the liquid becomes nearly colourless. Under similar conditions, the solar oil solution gives a strong yellowish-brown precipitate, but still remains yellow. A solution of butyrate in a mixture of the two oils, gives on cooling a yellowish-brown, and above this a greenish-blue precipitate; the supernatant liquid is pale-yellow. These reactions are sufficiently sharp in the case of American petroleum and solar oil of the Weisenfels district; it has not been ascertained whether they are applicable to other varieties. J. T.

**Detection of Adulterated Essential Oils.** By H. W. LANGBECK (*Pharm. J. Trans.* [3], 15, 309—310).—The author has devised a method for the detection of adulterated essential oils, based on the fact that salicylic acid dissolves in essential oils, but more readily in those containing oxygen than in those that do not. For example, oils from *Labiatae* dissolve more of it than oils from *Umbelliferae*, and the latter more than oils from *Coniferae*, &c. His method is as follows: 0.05 gram salicylic acid is put in a tared tube, the oil to be tested is added drop by drop, and shaken until a clear solution is obtained, the tube with contents is then weighed, the increase giving the relative solubility. Having examined several pure oils and mixtures of known composition, the author has constructed a table of solubilities for reference. All essential oils contain water from the steam distillation, which in course of time becomes converted into hydrogen peroxide; the age of an oil may therefore be tested in the following manner: the oil is shaken with an equal volume of water, and the water is then tested with iodised starch-paper; this is not discoloured by fresh oils, but is so to a more or less degree, according to the age of the oil, which can thus be

ascertained by comparison with an oil of known age. The test-paper is coated with a mixture of 1 part of starch, and 2 of potassium iodide, to 100 of water.

D. A. L.

**Estimation of Hydrocyanic Acid.** By L. SIEBOLD (*Pharm. J. Trans.* [3], 15, 158—159).—The following method is suggested to minimise the chances of error in the estimation of hydrocyanic acid by Liebig's process. A preliminary rough determination is first made, using a large excess of standard soda; then a second titration is made with a very slight excess of soda, and the hydrocyanic acid, to avoid loss by volatilisation, is run from a burette into the soda. When using the U.S.P. method (*Abstr.*, 1883, 1174) the hydrocyanic acid should be added to the mixture of magnesia and potassium chromate, and the silver nitrate then run in quickly. Magnesium, calcium, and barium carbonate can be used instead of magnesia, but the change is not recommended.

D. A. L.

**Estimation of Methyl Alcohol in Ethyl Alcohol.** By VAN DE VYVERE (*Chem. Centr.*, 1884, 69).—The author employs the property possessed by methyl alcohol of forming a compound with calcium chloride, which is not decomposed at 100°, but is decomposed by the addition of water. The alcohol to be treated is distilled over anhydrous sodium carbonate on the water-bath, and the volume of the distillate is determined. A portion of the distillate is allowed to remain over an equal weight of anhydrous calcium chloride for 24 hours. The ethyl alcohol is then distilled off. The residue, when treated with water and distilled, yields a mixture of methyl alcohol and water.

J. T.

**Detection of Fusel Oil in Spirituous Liquors.** By B. RÖSE (*Arch. Pharm.* [3], 23, 62).—To detect and estimate fusel oil in spirits, the author agitates 100 c.c. of the liquid (brought to the strength of 50 per cent. alcohol) with 20 c.c. of chloroform in a graduated tube of special form. After two minutes' agitation with 50 per cent. solution of pure ethyl alcohol, the chloroform will form an upper layer, measuring 37.1 c.c. But if only 1 per cent. of fusel oil be contained in a spirit similarly treated, this layer will measure 38.9 c.c. In general the increase of the volume of the chloroform layer for a given percentage of fusel oil must be previously determined by experiment with the particular spirit to be tested.

R. R.

**Sodium Nitroprusside as a Reagent for Sugars.** By K. LASCH (*Chem. Centr.*, 1884, 893—894).—An aqueous solution of 2 parts of the reagent with 1 of potash gives a strong persistent brownish-yellow coloration with a solution of cane-sugar. The same reagent applied to a solution of grape- or invert-sugar, heated to 60°, gives a brown colour, which immediately disappears on shaking, and a permanent coloration is not obtained until all the grape-sugar is destroyed. Towards the end of the reaction, the colour disappears more slowly, and the operation is accelerated by heating at 80°. The reaction is extremely sensitive, so that the end of the process is easily observed.

Experiment shows that 1 gram pure cane-sugar when converted into invert-sugar, requires 10.980 grams of the salt. To determine the invert-sugar in a sample, 1 gram is taken, dissolved in 40 grams water, warmed to 70°, and the standard solution is added until the brown colour no longer disappears after 15—20 seconds' shaking. In another portion, the cane-sugar is first converted into invert-sugar and after neutralisation with sodium carbonate the titration is made as above. The author has found the results to be accurate to  $\frac{1}{10}$  per cent. He has only found two organic acids occurring in beetroot juice, which affect the reagent, namely oxalic and tartaric acids. This juice therefore must be titrated after treatment with lead acetate. J. T.

### Determinations of Lactose in Milks by Optical Methods.

By H. W. WILEY (*Amer. Chem. J.*, 6, 289—302).—The usual method of determining milk-sugar requires a great deal of time, and a rapid and trustworthy optical method is very desirable. The author recommends precipitating the casein with some suitable reagent, and optically determining the lactose in the filtrate, taking the specific rotatory power of milk-sugar at  $[\alpha]_D = 52.5$ . Various albumins are present in milk, all of which turn the plane of polarisation to the left. To remove these, several reagents were tried, basic lead acetate, an acid solution of mercuric nitrate, acetic, nitric, and sulphuric acids, and solutions of various salts being among the chief. The best results were obtained with basic lead acetate and mercuric nitrate in certain proportions. For 50 or 60 c.c. of milk use 1 c.c. of lead solution, sp. gr. 1.97, or 1 c.c. nitric acid solution of mercuric nitrate (previously diluted with an equal volume of water). The results obtained by the use of the lead solution are lower than those given by mercuric nitrate, and this may be due to the fact that the filtrate from the former contains more albuminoids than the filtrate from the latter.

In testing the value of these analyses, they were always compared with results obtained by the ordinary method. The mean sugar percentage of the whole analyses are: by alcohol (ordinary method, 65 analyses) 4.32; lead acetate, cold (53 analyses), 4.34; lead acetate, hot (64 analyses), 4.38; mercuric nitrate, cold (61 analyses), 4.58; mercuric nitrate, hot (24 analyses), 4.63. If the milk-sugar exists in the anhydrous state after extraction by alcohol, the percentage of it in the hydrated state would be 4.61, which closely agrees with the results obtained with mercuric nitrate.

For the mercuric nitrate solution, the author dissolves mercury in double its weight of nitric acid, of sp. gr. 1.42, and adds an equal bulk of water; or a solution of mercuric iodide in acetic acid may be used, obtained by mixing potassium iodide, 33.2 grams, mercuric chloride, 13.5 grams, strong acetic acid, 20 c.c., and water, 640 c.c.; of this 25 c.c. should be used for 50 c.c. of milk.

In carrying out analyses by the optical method, the room and the milk should be kept at a constant temperature. If the sp. gr. of the milk be 1.026, or nearly so, measure out 60.5 c.c. into the sugar flask; add 1 c.c. of mercuric nitrate solution, or 30 c.c. mercuric iodide solution, and fill up to 102.4 c.c. The precipitated albumin occupies a volume of about 2.4 c.c. Hence the solution is really

100 c.c. If the sp. gr. is 1.030, use 60 c.c. of milk, and for sp. gr. 1.034, use 59.5 c.c. Fill up to mark, shake well, filter, and polarise.

J. K. C.

**"Dry Extract."** By JAY (*Bull. Soc. Chim.*, **42**, 217).—The "dry extract," which is an article of commerce, is used for sophisticating wine. Its chief constituents are glucose (28.7 per cent.), glycerol (38.4 per cent.), tannin (4.1 per cent.), dextrin (3.14 per cent.), and boric acid (4.27). The presence of this extract in wine may be detected by evaporating and igniting the residue, when the boric acid is revealed by the green tinge of the flame, and the glucose may be detected in the wine by polarimetrical examination.

W. R. D.

**Estimation of Wine Extract.** By C. WEIGELT (*Zeit. Anal. Chem.*, **24**, 26—30).—The author discusses the relation existing between the sp. gr. of the solution and the weight of the extract, and a tabular statement is appended, showing that, in wines of very various qualities and specific gravities, the amount of extract deduced from the indirect method agrees satisfactorily with that obtained by the direct method. The percentage of extract can also be calculated by finding the sp. gr. from Balling's saccharimetric tables. S. R.

**Melting Point and Separation of Mixtures of Phenylacetic and Hydrocinnamic Acids.** By H. SALKOWSKI (*Ber.*, **18**, 321—326).—The melting points of mixtures of these acids are shown in the accompanying table:—

Phenylacetic acid, per cent. . .	100	90	80	70	60	50
Melting point.....	77°	71.5°	65.5°	58°	50°	39.5°
Phenylacetic acid, per cent. ....	40	35	30	20	10	
Melting point.....	26.5°	21°	27°	33°	41.5°	

The amounts of the two acids present in admixture can be approximately determined from the melting point, when the latter is above that of hydrocinnamic acid (47.5°), whilst in cases where the melting point is below that temperature, the effect on the melting point of the addition of a small quantity of phenylacetic acid will indicate whether the mixture contained more or less than 35 per cent. of the latter, and so show which part of the table to refer to.

A. J. G.

**Testing Peruvian Balsam.** By P. MACEWAN (*Pharm. J. Trans.* [3], **15**, 236—239).—With regard to the preliminary tests for impurities in Peruvian balsam, the author makes several notes, adverse and otherwise. He considers the sp. gr. a useful indication, it should be about 1.137 to 1.150 at 15.5°. When the U.S.P. sulphuric acid test is used, and the balsam is washed first with hot and then with cold water, it does not harden even if quite pure; the presence of 15 per cent., or upwards, of copaiba decomposes the sulphuric acid, with evolution of sulphurous anhydride and fumes. The ammonia test serves for the detection of ordinary resin, by causing abundant frothing. Flückiger's lime test, and Grote's modification of it, do not fulfil their objects, although oil may be detected by the latter. The best method

of testing the balsam is by successive exhaustion with (1) light petroleum, (2) carbon bisulphide, (3) ether. The first solvent takes up *cinnameïn*, the residue from the evaporation of the solution, changes colour when treated with nitric acid; that from pure balsam becomes pale green, changing slowly to violet, which darkens ultimately to chocolate-brown. When impurities are present, the following colour changes take place: with storax, pale-green darkening to opaque-green; benzoïn, same as pure balsam, but the violet is permanently pale and bright; with colophony, bright emerald-green; and with copaiba, an intense blue coloration. The last two are very distinctive; the storax and benzoïn colorations are of themselves not sufficient indication of the adulterants. The carbon bisulphide extracts the *resin*, whilst the ether completely dissolves the *styracin*, and the insoluble residue is *woody matter* and a little resin.

D. A. L.

**Soxhlet's Aræometric Butter-fat Estimations.** By M. SCHMÖGER (*Bied. Centr.*, 1885, 70).—According to Fleischman, if sea sand is employed in the estimation of the butter-fat, the results are 0·2 per cent. too low; but if, instead of the sand, gypsum, silica, or precipitated chalk are used, the results are correct. With the object of assisting the separation of the ether, instead of cooling the skim-milk for 24 hours with ice, the author has added potassium or sodium sulphates, but the results are not satisfactory, necessitating the employment of a correction for error.

E. W. P.

**Basic Lead Acetate as a Test for Olive Oil.** By S. S. BRADFORD (*Chem. News*, 51, 57).—When pure oil is shaken in the cold with a solution of basic lead acetate, immediate saponification ensues. If, however, any foreign oil is mixed with the olive oil saponification does not take place, and when cotton-seed oil is the impurity, a red coloration is produced.

D. A. L.

**Quantitative Separation of Rosins and Fats.** By T. GLADDING (*Chem. Centr.*, 1884, 38, 716).—0·6 gram of the fatty acid adulterated with rosin, is dissolved in 20 c.c. of alcohol of 95 per cent., and the solution mixed with a trace of phenolphthaleïn, rendered alkaline with alcoholic potash and boiled. After cooling, the liquid is made up to 100 c.c. by addition of ether, and well shaken, 1 gram of very finely powdered silver nitrate is added, and the whole well shaken for 10 or 15 minutes, in order to allow the flocculent precipitate of oleate and stearate of silver to collect. As soon as the solution is clear, 50—70 c.c. are placed in a 100 c.c. glass, more powdered silver nitrate added, and the whole again well shaken, in order to precipitate the small amount of fatty acids still held in solution. The clear liquid is then mixed with 20 c.c. of diluted hydrochloric acid, and an aliquot part of the ethereal solution is evaporated; the residue, which consists of rosin with a little oleic acid, is dried in the steam-bath and weighed.

10 grams of the ethereal solution retain 0·0024 gram oleic acid. This coefficient can be used in correcting the results of the analysis.

H. P. W.

**Caramel.** By C. AMTHOR (*Zeit. Anal. Chem.*, **24**, 30—33).—Paraldehyde destroys the colour of an alcoholic solution of caramel, and forms at the same time a brown precipitate. With pure white wine, natural wine, and extract of raisins, paraldehyde gives a white precipitate; the caramel precipitate can be further identified by its reaction with phenylhydrazine. A solution containing 2 parts of phenylhydrazine hydrochloride with 3 parts of sodium acetate dissolved in 20 of water, gives with solutions of caramel, a brown precipitate, soluble in warm ammonia or weak caustic soda to a red liquid, and reprecipitated from the alkaline solution by the addition of hydrochloric acid. The precipitate is soluble in concentrated hydrochloric or nitric acid, but is reprecipitated on diluting with water. Alcohol similarly dissolves it, and water reprecipitates it after some time. The method adopted in testing for caramel in white wines or spirits is as follows: 10 c.c. of the liquid (if a wine 10—15 c.c. of alcohol are first added) are placed in a tall glass cylinder, and 30—50 c.c. of paraldehyde solution added, together with sufficient absolute alcohol to make the two liquids mix. After 24 hours, the precipitate is collected, washed with alcohol, and dissolved in warm water, again filtered, and the liquid evaporated to 1 c.c. The intensity of the colour is a measure of the amount of added caramel. With very small quantities, it is best to evaporate the solution by placing it in the receiver of an air-pump over sulphuric acid. The solution must not be warmed, or a caramel-like precipitate is obtained even with the purest wines. The concentrated solution of the paraldehyde precipitate can then be treated with phenylhydrazine solution, when the caramel-phenylhydrazine precipitate will be thrown down. If the solution is weak, it at first only becomes turbid, but the precipitation is complete after 24 hours. Any resinous bodies present can be dissolved out by shaking with ether, which has no action on the precipitate. Phenylhydrazine gives no precipitate with natural wines, and thus differs from paraldehyde. Wines containing a large percentage of sugar should be diluted before trying the above reactions. S. R.

**Estimation of Nicotine.** By E. SCHEFFER (*Pharm. J. Trans.* [3], **15**, 425—426).—The author has investigated the method for the estimation of nicotine by means of Mayer's solution (potassium mercuric iodide). He employed solutions of pure nicotine of known strength, and a test solution containing 0.01354  $\text{HgCl}_2$  and 0.0498 KI per c.c. He draws the following conclusions:—1 c.c. of Mayer's solution = 0.0081 nicotine; the crystalline precipitate has the composition  $\text{HgI}_2 \cdot \text{C}_{10}\text{H}_{11}\text{N}_2(\text{HI})_2$ , it is soluble in potassium iodide, and therefore nicotine exists in the solution after Mayer's solution has ceased to give a precipitate. The resinous precipitate which is sometimes obtained contains more mercuric iodide than the above precipitate, and when it is formed, more of Mayer's solution is required to complete the reaction than when the precipitate is crystalline. Dilute solutions take more of Mayer's solution, owing to the fact that the precipitate formed is resinous. Therefore, to avoid the formation of resinous precipitate, and to obtain correct results, the solution to be

tested should not contain less than 0.5 per cent. nicotine, to which 1 drop of strong hydrochloric acid should be added for each 10 c.c. employed, and a large quantity of Mayer's solution should be mixed in at once, and brisk stirring continued until the crystalline precipitate commences to form. The amount of nicotine in solution after precipitation is complete may be calculated from the quantity of mercury then remaining in solution.

D. A. L.

**Detection of Strychnine and other Alkaloids in Cases of Poisoning.** By T. CHANDELON (*Zeit. Physiol. Chem.*, 9, 40—48).—

The usual mode of isolating strychnine in poison cases is that of Stas: the following process is recommended as more convenient and very accurate. The intestines, &c., are cut up very finely, mixed with an equal weight of well burned gypsum, and the whole well rubbed in a mortar until a perfectly homogeneous mass results. This sets in 4—5 hours, when it is easily broken up into fragments. These are dried either in a water- or air-bath at 70°, pulverised, and the powder boiled with 90 per cent. alcohol to which some tartaric acid is added. When the powder has been boiled for an hour in a large flask connected with a reflux condenser, it is filtered, and the residue washed with hot alcohol. If the reaction of the filtrate is not acid enough, tartaric acid is added and the whole distilled. When the bulk of the alcohol is distilled off, the remainder is expelled by evaporation to dryness on the water-bath, the residue is taken up with a little boiling water, and left to cool in order to separate the fat. The filtrate, which should be about 20—25 c.c., is made decidedly alkaline with soda and transferred to a large watch-glass, mixed with gypsum, allowed to set, powdered, dried in an exsiccator, and then extracted with chloroform in a large Soxhlet's apparatus. The chloroform extract is brought to a small volume, 10—15 c.c., filtered if necessary, and the extract treated with an equal volume of a saturated solution of oxalic acid in ether. Fine acicular crystals of strychnine oxalate soon appear; the oxalate is collected on a filter, washed with a mixture of equal parts of alcohol and chloroform, dried and dissolved in the least possible quantity of water, and the strychnine precipitated by addition of ammonia.

By this method, the author has recovered strychnine from a frog killed by a subcutaneous injection of 0.01 gram, from the liver of a rabbit killed by subcutaneous injection of 0.04 gram of the sulphate, and from the stomach of a cat killed by eating flesh containing 0.03 gram of strychnine.

Experiments show the process to be very accurate. As chloroform is a solvent of most vegetable alkaloids, it is evident that this process or a slight modification of it can be used for the isolation of such of them as are precipitated by an ethereal solution of oxalic acid. The author made experiments with brucine, narceine, papaverine, thebaine, morphine, aconitine, atropine, hyoscyamine, veratrine, nicotine, conine, and colchicine, two of these, morphine and colchicine, were not soluble in chloroform, the others were completely precipitated as oxalates. The precipitate took some hours to form in the case of strychnine, brucine, narceine, codeine, nicotine, and conine, for the remainder



24 hours were necessary. The precipitate was crystalline in every case except that of aconitine, which was amorphous.

In the case of brucine, nicotine, veratrine, and atropine, which are not completely precipitated by ammonia, the oxalate is dissolved in alcohol, the oxalic acid is precipitated by a little alcoholic potash, filtered off, and the potash removed by a stream of carbonic anhydride; after frequent filtration, the alcohol is allowed to evaporate spontaneously, and the pure alkaloid remains. J. F.

**Detection of Colocynthein, Elaterin, and Bryonin.** By E. JOHANNSON (*Zeit. Anal. Chem.*, **24**, 154—157).—Colocynthin when heated with dilute sulphuric acid yields colocynthein, elaterin, and bryonin.

Colocynthin is soluble in water and alcohol; it gives an orange colour changing to red with concentrated sulphuric acid, a cherry-red coloration with sulphuric acid containing molybdic acid, a blood-red coloration turning blue at the edge with sulphuric and vanadic acids, a yellow coloration with alcohol and sulphuric acid, distinguishing it from solanine and solanidine, and a yellow coloration with sulphuric and selenic acids; moistened with phenol and a drop of sulphuric acid, it gives a blood-red coloration changing to orange.

Colocynthein is not as soluble in water as colocynthin, it is only sparingly soluble in light petroleum, but easily in benzene. With molybdic and sulphuric acids, it remains at first unchanged, but finally becomes a dirty cherry-red. With vanadic and sulphuric acids, its reactions resemble those of colocynthin. Colocynthin and colocynthein may be separated by shaking the acid solution with benzene which dissolves the colocynthein, and afterwards with ethyl acetate which dissolves the colocynthin.

Elaterin is insoluble in water; it is sparingly soluble in cold, but easily in boiling alcohol; it crystallises in colourless, shining, six-sided plates. With concentrated sulphuric acid, it gives a pale yellow coloration, becoming red at the edges after some time, and finally cherry-red. Molybdic and sulphuric acids give a fugitive green colour. Phenol and sulphuric acid give a momentary red coloration. Vanadic and sulphuric acids give a fine blue, changing to a bright green colour. Selenic and sulphuric acids give a red colour not so intense as that produced by concentrated sulphuric acid alone. Alcohol and sulphuric acid give on warming only a faint yellow colour. When evaporated on the water-bath, and then treated with sulphuric acid, a violet-red coloration is obtained. The elaterin reactions are slow, and, with the exception of the characteristic vanadic and sulphuric acids test, unsatisfactory.

Bryonin, in its reactions, resembles colocynthin and elaterin, and is readily soluble in water and alcohol. Selenic and sulphuric acids give a dirty cherry-red, and vanadic and sulphuric acids a blue-violet colour. S. R.

**Detection of Berberine, Hydrastine, and Oxyacanthine.** By L. V. HIRSCHHAUSEN (*Zeit. Anal. Chem.*, **24**, 157—163).—Berberine

gives with phosphomolybdic or phosphotungstic acid a yellow amorphous precipitate, with potassio-mercuric iodide the precipitate is greenish-yellow, with potassio-bismuthic iodide orange-red, with potassio-cadmium iodide bright yellow. The precipitates formed with platinic chloride, auric chloride, mercuric chloride, picric acid, and potassic bromide are all of a yellow colour, and are easily obtained with 0.01 mgrm. of the alkaloid. Potassium dichromate gives a yellow amorphous flocculent precipitate with 0.02 mgrm. An alcoholic solution containing 0.01 mgrm. berberine sulphate, gives with a solution of iodine in potassium iodide an immediate crystalline precipitate of a green colour if the reagent is added gradually. Potassium ferrocyanide precipitates a salt of the alkaloid in yellow needles. Concentrated pure sulphuric acid, when added to a small quantity of the dry salt, gives a yellow coloration darkening to olive-green and finally disappearing. Molybdic and sulphuric acids give an immediate yellow colour, changing through dark-brown to violet-brown. Vanadic and sulphuric acids give a fine violet, and selenic and sulphuric acids a bright yellow colour with 0.01 mgrm. of the salt. Chlorine water gives a blood-red coloration with 1 mgrm. of berberine sulphate, but if the salt be first dissolved in a few drops of a 33 per cent. solution of hydrochloric acid, the colour is produced with 0.01 mgrm. of the salt. A crystal of potassic nitrate and the dry salt when moistened with concentrated sulphuric acid, give a brown-red passing to a fine orange-yellow. If potassium dichromate be substituted for the nitrate, the colour is more of a violet tint at first, and finally assumes a brownish-yellow hue. Phosphoric acid gives a yellow colour. With sugar and sulphuric acid, a yellow coloration, changing through green to black is produced. Bromine-water precipitates an orange-yellow bromide which rapidly loses its colour. Berberine is only sparingly soluble in chloroform, and not at all in petroleum, ether, or benzene. Hydrastine gives with phosphomolybdic acid a bright lemon-yellow precipitate; with phosphotungstic acid, potassio-cadmium iodide, or potassio-mercuric iodide, white precipitates; and with potassio-bismuthic iodide and potassium dichromate, orange precipitates. With 0.1 mgrm. of the alkaloid a solution of iodo-potassium iodide gives a deep brown flocculent precipitate. Vanadio-sulphuric acid gives a beautiful rose-red colour which slowly disappears. A crystal of potassium dichromate and sulphuric acid give a golden-yellow colour, changing to brown and green. Chlorine-water gives no coloration, even in the presence of hydrochloric acid. Bromine-water added to a solution of hydrastine in strong sulphuric acid gives an immediate orange precipitate. Hydrastine is insoluble in light petroleum, but the greater part dissolves in benzene.

Oxyacanthine gives white precipitates with potassio-mercuric iodide, tannic acid, and potassio-cadmium iodide; orange precipitates with picric acid or potassio-bismuthic iodide, and a deep brown precipitate with iodo-potassium iodide. Molybdic and sulphuric acids give an immediate violet coloration, changing to yellowish-green at the edges.

Oxyacanthine is not extracted from acid solutions by light petroleum or benzene, and only sparingly by chloroform. S. R.

**Detection of Sanguinarine and Chelidonine.** By A. v. KÜGELGEN (*Zeit. Anal. Chem.*, **24**, 165—166).—Concentrated sulphuric acid gives with 0.1 mgrm. of sanguinarine, a blue-violet coloration, changing after several hours to a dirty green. Sulphuric and molybdic acids give a violet colour with a tinge of red resembling, but somewhat lighter than, the corresponding morphine reaction; after an hour, the colour becomes brown and eventually green. Vanadium sulphate gives a bluish-violet colour, which turns bluish-black on standing. Selenic and sulphuric acids do not give so intense a violet colour as is produced when sulphuric acid alone is added. 0.02 mgrm. of the alkaloid in a few drops of dilute sulphuric acid (1 of acid to 50 of water) gives precipitates with tannin, bromo-potassium bromide, phosphotungstic acid, iodo-potassium iodide, and phosphomolybdic acid; and a turbidity with picric acid, potassio-mercuric iodide, potassio-cadmium iodide, potassio-bismuthic iodide, and gold chloride. Sanguinarine is not extracted from its acid solutions by light petroleum, and only sparingly by benzene and chloroform.

*Chelidonine.*—0.5 mgrm. of this alkaloid gives with sulphuric acid at first a pale-green colour, changing to brown edged with red or violet. The violet colour is only observed in strong solutions. Sulphuric and molybdic acids give a green colour, changing to blue, brown, and black. Selenic and sulphuric acids, after a time, give a pale-green, which changes, on warming, to a red-brown. Sulphuric acid and potassium dichromate give similar reactions. Vanadic sulphate gives an intense emerald-green coloration, which turns to a bright blue, changing to a dark green. Potassium nitrate and sulphuric acid give a green, changing to a blue, and finally becomes fawn-coloured (in small quantities, the colour is steel-blue). Bromine and sulphuric acid give a red-brown with green streaks. Sugar and sulphuric acid give a rose-violet colour, changing to cherry-red and blue-violet. Chelidonine is not extracted from an acid solution by light petroleum, only slightly by benzene, but better by chloroform. S. R.

**Estimation of Chlorine in Human Urine.** By W. ZUELZER (*Ber.*, **18**, 320—321).—Chlorine in urine cannot be estimated directly by Mohr's method, on account of other constituents—uric acid, colouring matters, &c.—also being precipitated, and so rendering the results too high. The author recommends the following process:—10—15 c.c. of the urine is acidulated with nitric acid and precipitated with silver nitrate; the silver chloride formed is dissolved in ammonia, the silver precipitated by colourless freshly prepared ammonium sulphide, excess of sulphide removed by cadmium nitrate, and an aliquot part of the liquid filtered, acidulated with nitric acid, neutralised with calcium carbonate, and titrated by Mohr's method.

A. J. G.

**Simple Method of Estimating Nitrogen in Urine.** By E. PFLÜGER and K. BOHLAND (*Pflüger's Archiv*, **35**, 454—466).—As the results of numerous experiments, the authors recommend the following modification of Kjeldahl's process (*Zeit. Anal. Chem.*, **22**, 366):—5 c.c. of urine of average concentration are measured into an Erlen-

meyer's flask of about 300 c.c. capacity, together with 10 c.c. of concentrated sulphuric acid and 10 c.c. of Nordhausen acid, and the flask and its contents placed on wire gauze and heated over a large Bunsen flame until all water and gases formed are driven off; the heating is continued until the liquid assumes a clear yellow tint. The heating takes about 25—30 minutes. After cooling, the contents of the flask are diluted to about 200 c.c., and the ammonia formed is estimated by distillation with soda in the usual manner. The whole analysis can be effected in an hour (comp. Kreusler, this vol., p. 434).

A. J. G.

**Estimation of Nitrogen in Urine.** By K. BOHLAND (*Pflüger's Archiv*, **35**, 199—276).—It has been long known that the results obtained by the titration of the carbamide in urine by Liebig's method did not accord with the determination of the total nitrogen in the urine, the amount of nitrogen deduced from the titration being in many cases larger than the total amount present. The author gives details of the analyses of 63 samples of urine, the nitrogen being calculated from the results of the titration by Pflüger's modification of Liebig's method, and also determined directly by combustion with copper oxide. In 16 cases, the nitrogen was also determined by Will and Varrentrap's method, with results agreeing closely with those obtained by combustion with copper oxide. In almost every case the nitrogen calculated from the titration exceeded the amount really present. The nature of the food taken appears to have a considerable effect on this difference. With human urine on a mixed diet, the titration gave an excess of from 7—10 per cent. of the total nitrogen; in one case only an excess of as little as 2.2 per cent. being observed. In many experiments with dogs, the same tendency to results in excess was noticed; an approximate agreement between the titration and direct nitrogen estimations being observed only after long feeding on a flesh diet. From these results it follows that the titration method cannot be employed in investigations on the income and output of the body, and that direct methods for the estimation of nitrogen will have to be exclusively employed.

A. J. G.

**Estimation of Alkalis in Urine.** By T. LEHMANN (*Zeit. Physiol. Chem.*, **8**, 508—510).—The estimation of alkalis in urine, according to Neubauer's method, is frequently inaccurate; the following process is recommended:—The quantity of urine taken for the determination depends on the sp. gr. With a urine of sp. gr. 1.020, 100 c.c. are taken; with those of higher sp. gr. but 50 c.c. are taken. The urine is poured into a platinum basin, a suitable quantity of ammonium sulphate is added (3—4 grams generally), evaporated to dryness and ignited; this operation is safer than when urine alone is ignited, and a greater heat may be applied, the sulphates not being volatile. Generally the ash is perfectly white; if grey, it is moistened with sulphuric acid and again ignited. It is dissolved in hot dilute hydrochloric acid, filtered, treated with baryta-water to alkaline reaction, and the alkalis determined in the usual way.

The separation of sodium and potassium chlorides requires some

care. Commercial platinic chloride always contains free acid which exercises a solvent action on the potassium platinochloride, it is therefore safer to evaporate the solution of the chlorides (after addition of the platinic salt) to complete dryness, moisten the residue with a few drops of water, and rub with a glass rod, add more water, and again evaporate to the consistence of syrup. Alcohol of 96 per cent. is then added, and the mixture stirred; after settlement of the precipitate, the supernatant fluid is decanted on to a filter, the crystals in the dish are washed in this way until the liquor passes over clear, then the residue itself is transferred to the filter with the usual precautions.

J. F.

**Apparatus for Estimating Carbamide.** By A. W. GERRARD (*J. Pharm.* [5], 11, 152).—The apparatus consists of an upright graduated jar, standing on a foot and tubulated at the bottom, while the top is closed by an india-rubber stopper through which passes a short tube terminated in a small piece of india-rubber tubing provided with a pinch-cock, and having a side tubulure, which is connected by a long piece of india-rubber tubing with a bottle containing solution of sodium hypobromite, together with a test-tube holding 5 c.c. of the urine to be examined. The tubulure at the bottom of the upright jar is connected, by means of an india-rubber pipe, with an open reservoir of water, capable of sliding up and down, so that the heights of the water within and without the jar may be accurately adjusted to the same level. The bottle containing the hypobromite being tilted, so as to allow the urine to mix with the solution, the nitrogen liberated by the decomposition of the carbamide forces the water in the jar up into the reservoir, and when the proper adjustments of level are made, the volume of nitrogen can be read off.

R. R.

**Liebig's Method for the Estimation of Carbamide.** By M. LUZZATTO (*Gazzetta*, 10, 251–256).—This process for the estimation of carbamide, owing to the inherent sources of error, has practically been abandoned in favour of others, for on the one hand the degree of yellow coloration, produced when sodium carbonate is used as an indicator, varies to a different degree, with even small alteration of excess of mercuric nitrate added; and on the other, the proportion of water involved in the reaction constitutes an important factor in its degree of accuracy. In this paper, the latter point is more particularly investigated, and a series of analyses given in a table. As the result, it may be stated that if the solution contains a proportion not greater than 1 per cent., the quantity of mercuric nitrate required is relative to the proportion of carbamide; but in the case of a higher percentage, a less proportion of mercuric nitrate is required than that indicated by Liebig. This was admitted practically by Pflüger, although his experiments on this point were hardly conclusive.

V. H. V.

**Microchemical Detection of Nucleïn, &c.** By B. LOEW (*Bied. Centr.*, 1885, 68).—The author has employed Zacharias's method for detecting nucleïn (*Abstr.*, 1884, 90), and does not find it absolutely satisfactory. Working with spirogyra, hardly a trace of blue color-

tion is to be detected; but the whole of the protoplasm is blued if the spirogyra has been previously soaked in potash solution. The method of procedure is to soak the spirogyra in a dilute solution of potash and potassium ferrocyanide for 12 hours, then for some hours in a mixture of potassium ferrocyanide and acetic acid, then wash with water, then in alcohol (60 per cent.), and finally to let it lie in dilute ferric chloride; after this a blue coloration is noticeable, parts darkly, parts lightly tinged; a darker bluing is obtained if, after the treatment in acidified potassium ferrocyanide and dilute alcohol, the chlorophyll is extracted by absolute alcohol. E. W. P.

**Separation and Estimation of Serum-albumin and Globulin by means of Magnesium Sulphate.** By O. HAMMARSTEN (*Zeit. Physiol. Chem.*, 8, 467, 502).—The accuracy of the author's method and of the deductions therefrom, having been contested by Burckhardt, he has undertaken fresh experiments to prove their correctness. Magnesium sulphate precipitates *all* globulin from solutions, but does *not* precipitate serum albumin; this is denied by Burckhardt. The question seems to depend on what each understands by serum albumin; the author takes it to mean albumin soluble in water, not precipitable by carbonic anhydride, dilute acids, alkalis, or neutral salts; Burckhardt, on his part, calling by that name the substance left in solution after dialysis and precipitation by a stream of carbonic anhydride. There is, however, present in the blood a third substance which is intermediate between globulin and true serum albumin; this is precipitated by magnesium sulphate, and belongs rightly to the globulin rather than to the serum albumin group. The author has stated (*Abstr.*, 1879, 472) that in addition to the paraglobulin then isolated by him, there might be other analogous substances present.

The author details numerous experiments, all confirmatory of his views, and showing that the substance obtained by Burckhardt, and believed by him to be serum albumin, was in reality a globulin. Globulin is distinguished from paraglobulin by its coagulation temperature and its rotatory power ( $47.2-48^\circ$ ) thus agreeing with the observations of Frederique (*Abstr.*, 1882, 74). J. F.

**Quantitative Estimation of Micro-organisms in the Air.** By W. HESSE (*Chem. Centr.*, 1884, 251).

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### Technical Chemistry.

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**Molecular Modifications of Silver Bromide.** By DE PITTEURS  
(*Chem. Centr.*, 1884, 411—412).—See this vol., p. 349.

**Combinations of Silver Salts with Colouring Matters.** By  
M. CAREY LEA (*Chem. News*, 51, 30).—See this vol., p. 350.

**Isochromatic Gelatin Plates.** By O. LOHSE (*Chem. Centr.*, 1884, 782).—The author in continuing his researches on the modification of colour sensitiveness of silver bromide, endeavoured to find some means of increasing its sensitiveness.

Various yellow dyes were tried: 0.02 gram of the dye was dissolved in 100 c.c. of water containing 10 per cent. of ammonia, and the plates used (Nelson's "extra rapid") dipped for two minutes in the solution, and dried. Diamidoazobenzene hydrochloride considerably increased the sensitiveness of the silver salt for yellow and green, so that in photographs of the solar spectrum a second maximum of action appeared between the D and *b* lines, whilst, as in the case of eosin, a spot of less activity was observed in the proximity of F somewhat near to G. The sensitiveness as well as the colour sensitiveness of silver bromide is strengthened by chrysanine nitrate in conjunction with ammonia, and plates prepared with this mixture gave a spectrum photograph, which extended into the ultra-violet on the one side, and past D on the other.

A dilute solution increases the sensitiveness still more: plates treated with a solution 100 c.c. of which contained 0.004 gr. chrysanine nitrate and 2 c.c. of liquid ammonia, showed a sensitiveness of more than twice that of the untreated plate. H. P. W

**Transferring Photographs on to Porcelain or Wood.** By V. PAVLOFSKI (*Chem. Centr.*, 1884, 37, 703—704).

**Drinking Water Supplies.** By E. REICHARDT (*Arch. Pharm.* [3], 23, 41—52).

**Antiseptics.** By RATIMOFF (*J. Pharm.* [5], 11, 83—90).—The author has determined the limits between which lie the minimum quantities of various antiseptics required to kill and to prevent the development of microbes and bacteria in certain media, namely, water containing fresh muscle cut into small pieces, fresh ox blood, and veal broth. These liquids were fertilised from three different sources: one by water that had been shaken up with a little earth; by a drop of blood from a recently dead animal ("*bactéries charbonneuses*"); and by very virulent blood ("*bactéries septiques*"). The results are tabulated at length in the original. R. R.

**Orthophenolsulphonic Acid, a New Antiseptic.** By F. VIGIER (*J. Pharm.* [5], 11, 145—152, and 214—217).—Of the three phenolsulphonic acids, the ortho-acid only has antiseptic and disinfecting properties in a marked degree. It is not as poisonous as phenol, as much as 10 grams having been taken in small doses in 24 hours without inconvenience. The subcutaneous injection of 2.8 grams proved fatal to a dog. It appears to be a powerful antiseptic, although it is exceeded in this respect by its sodium salt. R. R.

**New Conserving Agent for Milk and Butter.** By M. SCHRÖDT (*Chem. Centr.*, 1884, 67).—Busse (*Milchzeitung*, 1882, No. 33) described experiments made with a new antiseptic which he calls "hydrogen acid." The author obtained some of this agent, which



appears to consist of hydrogen peroxide with a little hydrochloric acid, about 2 per cent. of borax, and traces of sulphuric acid. The author compared the action of Busse's agent on milk with that of hydrogen peroxide; in both cases the milk first showed an acid reaction after 14 hours, the temperature being 11–16°. The author concludes that Busse's solution offers no advantage over pure hydrogen peroxide. J. T.

**Preparation of Nitrous Oxide.** By P. CAZENEUVE (*J. Pharm.* [5], 11, 67–73).—The explosions which sometimes take place in the preparation of this gas on the large scale, are explained by the fact that the decomposition of ammonium nitrate is an exothermic reaction, and that the large quantity of heat thus liberated added to that directly applied, is capable of causing the sudden decomposition of the whole mass of the salt. The process is often slow in beginning on account of the contained moisture, and hence the operator is apt to apply undue heat at first. Therefore, the salt should previously be dried in a capsule at a temperature below 200°, and the retort should be heated slowly until the disengagement of gas begins, when only a very gentle heat will be required, and the operation should not be pushed too far towards the end. That the recently prepared gas has an irritating odour and causes symptoms of asphyxia, whilst after standing for some days in the gasholder it becomes easier to breathe, is due to the well-known difficulty of completely removing small quantities of one absorbable gas from another, even when the absorbing solution is very energetic in its action. The author found that nitrous oxide even after slow passage through solutions of ferrous sulphate and of sodium hydrate, retained this irritating odour, which he traced to the presence of a little hyponitrous acid. But when the gas was several times shaken up in a test-tube with a solution of ferrous sulphate, the irritating odour was at once removed, and the same effect was produced by allowing it to remain 24 hours in the gasholder. The author recommends that the gas should in all cases be prepared a sufficient time beforehand. The diminution in the anæsthetic properties of the gas after remaining for a time in the gasholder, is due to the fact that the nitrous oxide always contains a little free oxygen and free nitrogen, and that during a prolonged stay in the gasholder, the water gradually absorbs the protoxide; the relative proportions of oxygen and of nitrogen are thereby so increased that the anæsthetic property of the gas is sensibly diminished.

The author has examined the liquefied nitrogen protoxide, prepared in Paris by Duflos, and in London by Barth, and sold in cast-iron bottles. He finds these products are chemically pure, and therefore their employment in dental practice offers great advantages.

R. R.

**Decomposition of Ammonium Sulphate by means of Sodium Sulphate.** By G. BLATTNER (*Dingl. polyt. J.*, 255, 252–256).—The author has made a series of experiments, their object being to test the correctness of the equation  $(\text{NH}_4)_2\text{SO}_4 + \text{Na}_2\text{SO}_4 = 2\text{NaHSO}_4 + 2\text{NH}_3$ , on which Carey and Hurter have based a patented process for

obtaining ammonia from ammonium sulphate. In the first trials it was sought to ascertain whether considerable quantities of ammonia remained in the hydrogen sodium sulphate produced, or whether the total amount of ammonia was expelled. In each experiment a known quantity of pure crystallised ammonium sulphate was dissolved in a small amount of water, evaporated on a water-bath to the consistence of a thin syrup, treated with a little more than its equivalent proportion of calcined sodium sulphate, and heated until the evolution of ammoniacal vapours had ceased. The following results were obtained :—

	Grams $(\text{NH}_4)_2\text{SO}_4$ used.	Grams $\text{Na}_2\text{SO}_4$ used.	Percentage of $\text{NH}_3$ found in $\text{NaHSO}_4$ .
Experiment 1....	20	25	5.0
„ 2....	10	13	6.8
„ 3....	40	50	1.5
„ 4....	40	50	1.2

In experiments 1 and 2 the mixture was subjected to a lower temperature than in trials 3 and 4, and a compound of ammonia was formed at the sides of the vessel, which explains the presence of more ammonia in the hydrogen sodium sulphate. A second series of experiments shows that only 65 to 70 per cent. of the ammonia is liberated, as such, from the ammonium sulphate employed, the remaining 35 to 30 per cent. being distributed in about equal proportions, partly as ammonia left in the residue, and as ammonia sublimed in the form of hydrogen ammonium sulphate, partly as ammonia lost by decomposition.

Whilst this communication was in the hands of the printers, the author became acquainted with the circumstance that the inventors of this process recommend that the decomposition of the ammonium sulphate should be effected by forcing a current of steam through the mixed salts, at a temperature high enough to prevent the condensation of the steam. By the use of this remedy it may be possible to avoid the loss of ammonia or reduce it to a minimum, a circumstance which the author intends to investigate.

D. B.

**Separation of Kainite from Rock Salt.** By G. F. LÖFASZ (*Dingl. polyt. J.*, 255, 258).—The author proposes to boil the crude kainite, contained in a sieve placed over a boiling pan, with a hot saturated solution of kainite. The kainite is thus broken up into a powder, which on repeated stirring, falls through the sieve, and is collected in the pan. When kainite powder ceases to pass through the sieve, the residue is removed from the solution, the sieve charged with a new supply of crude kainite, and the operation repeated. Provisions are made for preventing the burning of the solution to the walls of the pans, and removing the powdered kainite and the residue without stopping the process.

D. B.

**Recovery of Sulphur from Soda Waste.** By H. GROUVEN (*Dingl. polyt. J.*, 255, 206—208).—The soda residues from the Leblanc process are introduced into a kneading machine, mixed with about 10 per cent. of saw-dust and from 10—15 per cent. of hot

water. A stiff unctuous dough is obtained which is formed into tubes by compression. These are 250 mm. long, have an external diameter of 45 mm., and an internal diameter of 20 mm. They are put on frames placed under an open shed and subjected to the action of atmospheric oxygen. Oxidation ensues, which rapidly hardens the mass, so that after the lapse of two days, the tubes are brittle enough to be broken into pieces without falling to a powder. The mixture is then heated in retorts whilst treated with steam. 100 kilos. residues contain 8 kilos. carbon in the form of coke-dust, and 4 kilos. in the 10 kilos. sawdust added, making a total of 12 kilos. carbon, which require 18 kilos. water in the form of steam for its conversion into gas. During the decomposition of the carbon, carbonic oxide and hydrogen are formed in the interior of each piece of the prepared mass, in quantities sufficient to effect the complete reduction of the oxides of sulphur (thiosulphuric acid, tetrathionic acid, sulphurous acid, dithionic acid, and sulphuric acid) contained in the residues. Thus almost all the sulphur is converted into calcium sulphide, which, on exposure to heat and superheated steam, is decomposed into sulphuretted hydrogen and calcium oxide. The object of adding sawdust to the residues is to obtain a mass of considerable porosity, without which the steam process cannot be worked successfully. The residue left in the retorts contains from 87 to 90 per cent. of caustic lime, and is used for the preparation of mortar or for manuring purposes. D. B.

**Manufacture of Phosphate from Basic Slags, according to Scheibler's Method, as used in Schalke and Stolberg.** By R. HASENCLEVER (*Chem. Centr.*, 1884, 764—765).—The slags are roasted on large furnace hearths. According to quality, 1000 kilos. of slag require 100—130 of coal. The roasted mass is treated with steam, which converts the lime into calcium hydroxide, and so splits the slag up into a very fine powder, which is passed through sieves in order to get rid of pieces of iron, unaltered slag, &c. The powder is then treated with dilute hydrochloric acid (1 of acid to 10—15 of water) in quantity sufficient to dissolve the free bases, and those combined with silica and phosphoric acid. After allowing the insoluble matter to settle, the liquid is drawn off, and carefully prepared milk of lime is either added in sufficient quantity to precipitate the silica and phosphoric acid, or the solution is imperfectly neutralised, so that only earthy phosphates, and small quantities of iron and silica, are precipitated, whilst the excess of silica remains in solution. The precipitate is pressed, washed, dried, and sold under the name of "lime diphosphate." A product was obtained, containing 35—37 per cent. of phosphoric acid in form of "bibasic phosphate of lime," and this on ignition yields a product containing over 45 per cent. of phosphoric acid. H. P. W.

**Reversion of Phosphoric Acid by Heat.** By W. B. PHILLIPS (*Chem. News*, 51, 64).—The author's experiments illustrate the rapid reversion of the phosphoric acid of manufactured phosphates at elevated temperatures. The results given below are:—A, from the analysis of a manufactured phosphate, 24 hours after preparation;

B and C, analysis of the same phosphate after exposure at 90—100°, for 2 days and for 10 days respectively.

	Phosphoric acid, per cent.				
	Total.	Soluble.	Insoluble.	Reverted.	Available.
A .....	17·31	11·74	3·32	2·25	13·99
B .....	17·13	10·59	2·95	3·59	14·18
C .....	17·32	7·48	2·85	6·99	14·47

The apparent increase in the available and decrease in the insoluble in B and C, is attributed to the fact that these samples were more finely powdered than sample A. D. A. L.

**Portland Cement and its Adulteration.** By R. and W. FRESSENIUS (*Zeit. Anal. Chem.*, **24**, 66—71).—The name "Portland cement" should be confined to the product obtained by heating together lime and clay in definite proportions, and then finely powdering the product. When this is mixed with more than 2 per cent. of foreign matters such as gypsum, the authors contend that the application of the name "Portland cement to the mixture" is fraudulent. The authors consider that the nomenclature needs revision, and seek the cooperation of cement manufacturers for this purpose. Their tests furnish a ready means of distinguishing between the pure article and substitutes or mixtures (see Abstr., 1884, 876). S. R.

**Graphite Crucibles.** By J. C. BOOTH (*Chem. News*, **51**, 55, from *Amer. Chem. J.*).

**Deposition of Silver on Glass, &c.** By F. L. JAMES (*Pharm. J. Trans.* [3], **15**, 306).

**Crucible Steel.** By A. LEDEBUR (*Chem. Centr.*, 1884, 74).—Troost and Hautefeuille have shown that on melting steel in siliceous crucibles silicon is produced by the action of carbon on the material of the pot, and passes into the steel. Plumbago crucibles give more silicon than clay pots: for instance, bauxite crucibles with 9 per cent. carbon gave 0·144 per cent. silicon; chamotte crucibles with 28 per cent. carbon gave 0·274 per cent. silicon; and similar pots with 39·5 per cent. carbon gave 0·392 per cent. silicon. The presence of manganese in the charge also favours the reduction of silicon; thus steel with and without a ferromanganese in the charge, gave 0·49 and 0·24 per cent. of silicon respectively. Owing to the greater affinity between carbon and manganese than between carbon and iron, a steel poor in manganese, when melted in a plumbago crucible, loses carbon, whilst a steel rich in manganese takes up carbon from the crucible. J. T.

**Phosphorus in the Blast Furnace.** By G. HILGENSTOCK (*Chem. Centr.*, 1884, 239—240, 253—255).—The author in a paper read

before the Society of German Ironmasters gives numerous analyses of pig-iron and slag, and draws the following conclusions from his observations: 1. No appreciable amount of the phosphorus introduced is volatilised and carried off in the escaping gases. 2. Under certain conditions a considerable amount of the phosphoric acid in the charge escapes reduction, and passes as such into the slag. The amount thus going into the slag being the greater, the less reducing material, that is fuel, is present, and the lower the temperature; and the higher the percentage of phosphoric acid present in the charge. 3. The more phosphorus goes into the iron, the less silicon and carbon are found in it, other conditions being the same. It is not, however, the phosphorus as such that expels the silicon or carbon, but the phosphoric acid at whose cost the silicon and carbon are oxidised. 4. With a charge rich in phosphorus, the slag contains less phosphoric acid the more silica is present. 5. Carbon is the only reducing agent for phosphoric acid in the blast furnace, either directly or indirectly.

J. T.

**The Changes occurring in Barley during Malting, and in the Manufacture of Spirits.** By P. BEHREND (*Bied. Centr.*, 1885, 51—56).—*Removal of Organic and Inorganic Matter by Water.*—The quality of the malt for brewing purposes is much influenced by the water in which it has been soaked, for if this water removes too much of the phosphates and potash, the yeast is unable to develop thoroughly; the water, regarded chemically, is not the only factor to be considered, attention must also be paid to the time of soaking and the temperature. The experiments were made on three varieties of barley, and it was noted that the largest percentage of material was removed from the smallest grains, due to the fact that the surface exposed to the water is relatively larger in the small than in the large grain. The author found that about one half of the dry matter removed consisted of organic matter; this observation is directly opposed to that made by Mulder and Lermier, who found that the greater part of the extract consisted of organic matter. The practical outcome of the research is that barley must not be soaked too long else it will not germinate well, and the fermentation will be languid; more attention must be paid when small grained barley is malted than when the large sized is used.

*The Changes which the Nitrogenous Matter undergoes.*—The conversion of insoluble into soluble nitrogenous matter is very rapid, the soluble will increase six times by the end of nine days' malting. Hungarian and Saal barley were closely examined during malting, and analytical data are given showing the gradual conversion of albumin into soluble nitrogenous matter, the period of conversion extended over 209 hours; no free nitrogen was noticed. It was also found that the soluble nitrogenous matter did not consist wholly of amides, but that a part of the albumin became soluble without decomposition, and this the more rapidly, the quicker the malting—that is the formation of diastase—proceeded. Another piece of information gained of practical advantage is, that the length of the shoots is no indication of the extent to which the change of the albumin has gone.

*Changes of the Albuminoids in Cereals and Potatoes when Heated under Pressure.*—At high temperatures, the albuminoids are rendered soluble, amides being formed, consequently the feeding value of the waste products is much reduced; but, on the other hand, this conversion is no detriment to the growth of the ferment, which seems to flourish equally well on albumins as on amides. When heated at 140° in Lintner's digester for six hours the albuminoids of lupines suffer much change; there was an increase of nearly double of the non-albuminoids, whilst the albuminoid nitrogen soluble in water was increased by 13·9 per cent. In peas, soluble non-albuminoid nitrogen was increased from 35 to 87·8 per cent., and 36·6 per cent. of the insoluble albumin was made soluble. Maize and dari were also much affected. Experiments with potatoes showed that if they had been previously dried at 110°, a part of the albumin being thus rendered insoluble, the after heating by steam at a high temperature was incapable of restoring all the coagulated albumin to a condition of solubility. To ascertain whether working on the large scale produced the same effect on albuminoids, as the small laboratory experiments, maize and dari were heated in a Henze's steamer under a pressure of four atmospheres. The results obtained to a certain extent corroborated the original experiments, but the changes were not so marked. A short steaming dissolves the albumin, but long continued steaming converts albumin into amides. E. W. P.

**Preparation and Investigation of Starch.** By O. SAARE and others (*Dingl. polyt. J.*, 255, 209—213).—Saare has made a series of experiments as to the comparative yields of starch obtained with millstones or with rasping machines, the results being in favour of the use of millstones.

The same chemist has worked out a method for estimating the percentage of water in potato-starch, which is based on the sp. gr. of the starch. Thirty samples gave for the sp. gr. of perfectly dry potato-starch 1·650 as a mean, the maximum being 1·653 and the

Weight found.	Water, per cent.	Weight found.	Water, per cent.	Weight found.	Water, per cent.	Weight found.	Water, per cent.
grams.		grams.		grams.		grams.	
239·40	0	283·50	15	277·60	30	271·70	45
289·00	1	283·10	16	277·20	31	271·30	46
288·60	2	282·70	17	276·80	32	270·90	47
288·20	3	282·30	18	276·40	33	270·50	48
287·80	4	281·90	19	276·00	34	270·10	49
287·40	5	281·50	20	275·60	35	269·70	50
287·05	6	281·10	21	275·20	36	269·30	51
286·65	7	280·75	22	274·80	37	268·90	52
286·25	8	280·35	23	274·40	38	268·50	53
285·85	9	279·95	24	274·05	39	268·10	54
285·45	10	279·55	25	273·65	40	267·75	55
285·05	11	279·15	26	273·25	41	267·35	56
284·65	12	278·75	27	272·85	42	266·95	57
284·25	13	278·35	28	272·45	43	266·55	58
283·90	14	278·00	29	272·05	44	266·15	59

minimum 1.647. The figures in the subjoined table are based on these numbers. The estimation is conducted in the following manner: 100 grams of starch are rinsed into a tared 250 c.c. flask, which is then filled up to the mark with water and weighed at 17.5°. The weight of the empty flask is then deducted from this amount and the percentage of water corresponding to the difference found from the table (p. 618). The results are correct to 0.5 per cent. The method is applicable also to the estimation of water in moist starch, and may be used for testing the progress of the drying process in the drying chambers.

L. Bondonneau states that an error often arises in determining the dry matter in starch, by heating the latter too rapidly to 60°, in which case glutination takes place. If the starch contains acid, sugar is formed on drying. It is therefore proposed to expose neutral starch in thin layers to a temperature raised gradually to 60°, and to heat the mass at 110° for one hour after three hours' heating at 60°. If the starch is acid, it is mixed with water and a few drops of ammonia and dried at 40°. The temperature is then increased to 60° and 110° as in the former case.

D. B.

**Dry Distillation of Wood.** By M. SENFF (*Ber.*, 18, 60—65).—The author has made a series of careful experiments to compare the products formed (1) by the distillation of different varieties of woods; of woods from different parts of the same tree; and of the same wood in a healthy and diseased condition; (2) by the rapid and slow distillation of the same wood. The experiments were carried out with a horizontal cylindrical iron retort 60 cm. long and 20 cm. diameter. In the slow distillations, the retort was gradually heated, after the introduction of the wood, and the operation took about six hours: in the quick distillations, the retort was heated to a bright red heat before the introduction of the wood, and the operation was completed in about three hours. The wood was in all cases dried by long exposure to the ordinary air of the room. The following results were obtained: I. *Comparing Different Kinds of Wood.*—The total percentage yield of crude acetic acid, tar, gas, and charcoal was almost the same for all kinds of wood; but the percentage of acid in the crude acid varied considerably. The wood of exogens yielded much more acid than that of endogens; the trunks more than the branches; wood more than bark, and healthy more than diseased wood. II. *Comparing Rapid and Slow Distillation.*—Rapid carbonisation gives more gas but less total distillate and charcoal, a considerably smaller percentage of acid, and a much more hygroscopic charcoal.

L. T. T.

**Recovering the Waste Acids from Nitroglycerol Works.** By W. POETSCH (*Dingl. polyt. J.*, 255, 216).—On heating the waste acids, consisting of sulphuric and nitric acids and organic nitro-compounds, at 105°, decomposition of the nitro-compounds ensues, oxidation to carbonic anhydride taking place at the expense of the nitric acid which is present. During the reaction, enough heat is liberated to volatilise the remaining portion of undecomposed nitric acid and the lower oxides of nitrogen produced, pure sulphuric acid being left in the residue. The author uses a closed vessel of stone or lead,

having a perforated bottom 50 cm. above the bottom. The upper space is filled with stones or broken stoneware and heated by hot air. The waste acid is introduced in a thin stream through a funnel fitted into the cover of the vessel, and, passing over the hot stones, is decomposed. The nitrogenous vapours are led through an earthenware pipe to a cooling worm and collected in Wolff's bottles, air being introduced to oxidise the gases to nitric acid. The denitrated sulphuric acid flows through the perforated bottom and is run into receiving tanks.

D. B.

**Siamese Benzoin.** By E. HIRSCHSOHN (*Chem. Centr.*, 1884, 829).—Siamese benzoin has a milk-white fracture, and yields a light yellow powder.

The carbon bisulphide extract when evaporated and allowed to remain in the cold for a few days, yields a large quantity of crystalline matter. After repeated crystallisations from ether, perfectly colourless, nodular crystals are obtained; they have a distinct vanilla-like odour, and dissolve in carbon bisulphide, ether, benzene, chloroform, and alcohol. The crystals are insoluble in water, but melt on boiling to a yellow oily mass; the aqueous extract is acid and, on cooling, crystals separate (benzoic acid?). With alcohol a similar result is obtained; the crystals are soluble in caustic soda. Sumatra benzoin yields but little soluble matter when treated with carbon bisulphide; whilst 50 per cent. of Siamese benzoin is soluble, and 30 per cent. of fine crystals obtainable.

H. P. W.

**Yield of Butter from Fresh and Stale Cream.** By A. BRÜNIC (*Bied. Centr.*, 1885, 70).—Fresh cream when churned yields 2.079 per cent. butter, and in the butter-milk 1.311 per cent. butter is found, which can be removed by Swartz's process; whilst from the stale cream, 3.315 per cent. of butter can be obtained directly.

E. W. P.

**Manufacture of Lubricating Oil from Baku Naphtha.** By F. A. ROSSMÄSSLER (*Chem. Centr.*, 1884, 765—766).

**Purree or Indian Yellow.** (*Chem. Centr.*, 1884, 463.)—This colouring matter is employed in India for painting doors, walls, and railings, and less frequently for dyeing cloths. There are two sorts of purree, namely, mineral purree, imported from London, and animal purree, obtained from the urine of cows fed on mangrove leaves. The urine is heated to precipitate the dye which is collected, made into balls, and then dried first over a fire and finally in the sun.

A. K. M.

**Flesh Meal.** By L. ROUSSEAU (*Bied. Centr.*, 1884, 792).—This meal is frequently valueless, becoming rancid by reason of the decomposition of albumin and fat. To avoid this, the flesh must be freed from fat, nerves, &c., dried at 45°, and then washed with alcohol and ether. The washed flesh is then to be dried at 110° and powdered, after which it is perfectly odourless and will keep. Such a powder yields to acetic acid 57 per cent. of Mulder's proteïn, whilst other powders only yield 47.5 per cent., and moreover the albumin can be extracted by water.

E. W. P.



## General and Physical Chemistry.

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**Correction of a Former Paper on the Spectrum of Samarium.**  
By L. DE BOISBAUDRAN (*Compt. rend.*, 100, 607).

**Refractive Indices of Condensed Gases.** By J. DECHANT (*Monatsh. Chem.*, 5, 615—626).—If the solar rays pass through a slit, and thence through a moderately thick glass tube filled with water, whose axis is parallel to the slit, the line of light expands on either side into a spectrum. The spectra so produced show that certain rays in their passage through the tube undergo a maximum deviation conditioned by the various angles of incidence and refraction. It is here demonstrated that the equation for the maximum deviation is  $\tan \alpha - \tan \beta + \tan \gamma - \tan \delta = \theta$ , in which  $\alpha$  is the angle of incidence,  $\beta$  angle of refraction of glass,  $\gamma$  angle of incidence on the inner surface of glass, and  $\delta$  angle of refraction of liquid. As then  $\tan \gamma > \tan \delta$ , the refractive index of the liquid must be less than that of the glass, and as  $\tan \alpha > \tan \delta$ , the ratio of the external and internal radii of the tube must be greater than the refractive index of the liquid. The author has adopted this method for the determination of the refractive indices of condensed gases, as presenting some advantages over the methods used by Faraday, Brewster, and Bleekrode. The necessary preliminary observations are (1) the refractive index of the glass, (2) the mean deviation of the rays, and the ratio of the radii corresponding thereto. As regards the effect of temperature, it is observed that a comparatively slight variation produced a considerable change in the refractive index: it is thus necessary to screen off extraneous rays as far as possible. Further, to prevent interference fringes, one of the two spectra produced is suppressed. The value found for liquid sulphurous anhydride for the D line at 20° is  $n = 1.34$ ; a rise of temperature causes a decrease of deviation of about 0.0008: the value for liquid cyanogen, under the same conditions, is  $n = 1.318$ ; these numbers are practically identical with those obtained by Bleekrode and Brewster. The refractive index of liquid hydrogen sulphide is  $n = 1.374$ , with a variation of 0.00114 for each degree C, and of liquid chlorine  $n = 1.385$  with a variation of 0.00098 for each degree C. For hydrogen persulphide, whose refractive index is greater than that of glass, a slightly different method is used, based on the principle of the primary rainbow, the angle of incidence being so arranged that the rays are totally reflected at the surface of the glass and air. The value found is  $n = 1.546$  for the conditions above mentioned.

V. H. V.

**Explanation of the Colour Phenomena of Pleochroic Crystals.** By W. VOIGT (*Jahrb. f. Min.*, 1885, 1, Mem., 119—141).

**Determination of the Double Refraction of Minerals.** By MICHEL-LÉVY (*Jahrb. f. Min.*, 1885, 1, Ref., 179—180).—The author  
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describes methods for determining the double refraction of minerals, in the form of thin sections 0·01 to 0·03 mm. in thickness. In a thin rock section of this kind, crystals are distributed in all possible positions, and under crossed Nicols it is easy to discover the crystal sections which give the most distinct double refraction, since they exhibit the brightest colours.

B. H. B.

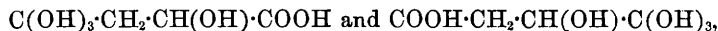
**New Apparatus for Measuring the Angle of the Optic Axes.**

By T. LIEBISCH (*Jahrb. f. Min.*, 1885, 1, Mem., 175—183).

**Optical Modifications produced in Crystals by the Action of Heat.** By W. KLEIN (*Jahrb. f. Min.*, 1885, 1, Ref., 175—178).—The author has endeavoured to find out what influence an unequal heating exercises on the optical properties of minerals. The observations were made with a Bertrand-Nachet microscope, and the minerals employed were :—Apatite, from Ehrenfriedersdorf; quartz, from St. Gothard; apophyllite, from the Seisser Alps in the Tyrol; zircon, from Ceylon; calcite, from Iceland; and cordierite, from Haddam. The optical properties of crystals of which the double refraction is positive, are modified in one direction, whilst those of crystals optically negative, are modified in the opposite direction. With this method, the optical character of uniaxial crystals may be determined. The experiments with biaxial crystals gave results analogous to those obtained with uniaxial crystals. In the case of cordierite, the angle of the optic axes increases, in proportion to the temperature, up to 200°. A plate of topaz treated in the same way presents phenomena exactly the reverse of those of cordierite.

B. H. B.

**Change of Specific Rotary Power under the Influence of various Solvents.** By G. J. W. BREMER (*Rec. Trav. Chim.*, 3, 162—165).—The author considers this change to be due to chemical change undergone by the substance in solution. Thus, for instance, a very concentrated solution of lævorotary malic acid has a dextrorotary action. This the author believes to be due to the formation of hydrates,



which are decomposed again by the addition of much water. Other similar cases are instanced.

L. T. T.

**Absolute Unit of Light.** By J. VIOLE (*Ann. Chim. Phys.* [6], 3, 373—407).—Adopting a suggestion of the author's, the International Conference of Electricians in 1882, resolved :—(1.) "The unit of each simple light shall be the quantity of light of the same kind normally emitted by 1 square centimetre of the surface of fused platinum at the temperature of solidification," and (2.) "The practical unit of white light is the quantity normally emitted from the same source." (See Abstr., 1884, 1447.) The present paper describes the method of practically realising this standard by the fusion of pure platinum, from which the light is allowed to pass upwards through properly disposed screens. The photometric measure is taken at the instant of solidifi-

cation; when the fused metal is allowed to cool, the luminous intensity diminishes rapidly at first, then more and more slowly; it afterwards becomes stationary, and then a kind of flash occurs at the moment of solidification before the decline of luminosity is resumed. The time for taking the measure is thus well defined, and, after a few trials, the operator is aware of the exact moment, without looking at the platinum.

By two independent methods—one for calorific, the other for luminous radiations, the author has verified the law of the cosine, the result, however, in the case of melted silver was somewhat higher (above  $60^\circ$ ) than the law indicated, being then 100·8 per cent., and at  $75^\circ$ , 104 per cent. The constancy of the radiations from the surfaces of solidifying silver and of platinum was proved by a specially constructed photometer, and the law of the more rapid increase of luminiferous power than of temperature was verified.

The intensity of the absolute unit is about 11 times that of an equal area of the flame of a normal Carcel lamp. Photometric measures of incandescent electric lamps agreed well with electric determinations of their intensities.

R. R.

#### Law of Emanation of Light from Incandescent Substances.

By W. MÖLLER (*Ann. Phys. Chem.* [2], 24, 266—281).—The law of cosines for the emanation of light from incandescent substances has been based hitherto rather on the analogy of light with heat rays, than on experimental evidence. By means of a simplified form of Wild's photometer, the author has given an empirical proof of the law, and has tested the relative intensity of the more important incandescent lamps. According to the theorem of Lambert in his *Photometria*, published in the middle of last century, the degree of illumination from an incandescent surface may be expressed by the formula  $T = \frac{iF \cos i_1 \cdot \cos e}{r^2}$ , in which  $i$  is the illumination of an unit surface,

$F$  the total area of the illuminating surface,  $r$  the distance of the illuminating from the illuminated surface,  $i_1$  and  $e$  the angle of incidence and emanation from the prism apparatus of the photometer. If  $i$  and  $F$  be kept constant, and  $r$  be made sufficiently large, so that  $r$  and  $e$  are practically constant for all points of the illuminating surface, then the formula becomes  $T = A \cos x$ , in which  $A$  is a constant, and  $x$  the angle at which the illuminating surface is inclined to the axis of the photometer. The method of experiment consisted, in outline, of the photometric comparison of two platinum foils rendered incandescent by the same electric current, the one of which was used as a standard, whilst the other was inclined at various angles to the axis of the photometer. It is thus demonstrated experimentally that the intensity of light and the cosine of the angles of inclination vary in exactly the same ratio; thus Lambert's theorem is empirically confirmed.

V. H. V.

**Galvanic Polarisation.** By E. PIRANI (*Chem. Centr.*, 1884, 7).—The author's result seems to show conclusively that the chemical nature of the electrode influences the amount of polarisation.

J. T.

**Products of the Electrolysis of Dilute Sulphuric Acid.** By F. RICHARZ (*Ann. Phys. Chem.* [2], **24**, 183—209).—The experiments of Faraday, Schönbein, and others have demonstrated that by the electrolysis of dilute sulphuric acid there are formed, besides electrolytic gas, hydrogen peroxide and ozone, to which Berthelot has recently added persulphuric anhydride,  $S_2O_7$  (Abstr., 1878, 469). In this paper, experiments are detailed, tracing the connection between the proportion of ozone, hydrogen peroxide, and persulphuric anhydride formed, and the conditions of the experiment. The observation of Schönbein that for the formation of a considerable quantity of hydrogen peroxide, a considerable electric intensity is required at the positive electrode, and a low temperature, was at first confirmed. But in the course of the research it was noticed that the mutual reduction of the hydrogen peroxide and the persulphuric anhydride at the negative pole (a probable assumption of Hoffmann and Berthelot) causes a quantity of hydrogen, corresponding with a certain quantity of oxidising or available oxygen, to disappear, and thus cause a deficit in the products of electrolysis. Thus the sum of the evolved electrolytic gas, of the oxygen evolved as ozone, and of the oxidising or available oxygen in the persulphuric anhydride, is always less than the volume of electrolytic gas, as calculated from the observed deviation of the tangent galvanometer. The author considers that this deficit is caused partly by the reduction of the persulphuric anhydride, and partly by the absorption of the electrolytic gas by the dilute sulphuric acid. By increasing the temperature, this deficit decreases, owing, firstly to the decrease of persulphuric anhydride formed, and secondly, to the diminution of solubility of the electrolytic gas. It is remarked incidentally that the proportion of persulphuric anhydride formed decreases with rise of temperature more rapidly than that of the ozone.

The influence of the duration and intensity of the current and also of the concentration of the acid on the relative proportions of the products of electrolysis is also discussed. It is shown that the proportion of persulphuric anhydride, ozone, and the deficit observed increases with the time of passage of the current, whereas an increase of intensity of current produces precisely the reverse result; this is in accordance with Wiedermann's observations. As regards the effect of concentration, the results given in tables show that with an acid containing 10—20 per cent.  $H_2SO_4$ , the proportion of oxygen as ozone and persulphuric anhydride, as also the deficit, is small, and no hydrogen peroxide is formed; with an acid containing 20—40 per cent., the proportion of oxygen as persulphuric anhydride and the deficit increases; with acids containing 40—90 per cent., the proportion of oxygen as ozone and persulphuric anhydride and the deficit decreases, whilst the proportion of hydrogen peroxide *pari passu* increases.

The author proposes to examine the important question of the effect of the electromotive force of polarisation on the formation of these peroxides.

V. H. V.

**Electrical Conductivity of Carbon Compounds.** By A. BARTOLI (*Chem. Centr.*, 1884, 785).—The conductivity was measured

by interposing small thicknesses of the solid or liquid to be tested in the circuit of a battery composed of 400 zinc and chromic acid cells. In the case of liquids, it was also determined by observing the rate of change of potential of a metallic ball immersed in the liquid. The results obtained were as follows:—All solid carbon-compounds are non-conductors if measured at some distance below their melting point. All hydrocarbons and their chlorine, bromine, iodine, or cyanogen derivatives, ethers, and ethereal salts are non-conductors when in the liquid state. Water, alcohols, acetone, aldehydes, acids, anhydrides, quinones, phenols, and amines and their derivatives containing negative radicles show unmistakeable signs of conductivity. The conductivity decreases with the increase in complexity of the molecule. Conductors, when dissolved in non-conducting media, form conducting solutions. Non-conducting liquids do not become conductors when heated, but the conductivity of conductors is increased by heat.

L. T. T.

**Determination of the Specific Heat of Uranium.** By A. BLÜMCKE (*Ann. Phys. Chem.* [2], 24, 263—266).—In a former paper, the author stated that his determination of the specific heat of uranium differed from that of Zimmermann, although these two physicists had worked conjointly on this subject. It is here explained that this difference arose from differences in scale readings. The mean of the specific heat determinations give a value of 0.028 at a temperature of 98.85°.

V. H. V.

**Specific Heat and Latent Heat of Fusion.** By O. EHRLHARDT (*Ann. Phys. Chem.* [2], 24, 215—258).—By means of an apparatus described at length in the original memoir, the author has made determinations of the specific heats and latent heats of fusion of halogen compounds of lead and silver, selected as substances of high melting point. The main results obtained were as follows:—

With an interval of temperature of from 0° to within 60 degrees of the point of fusion, the quantity of heat required to raise a unit weight of substance one degree is, for lead and silver chlorides and lead bromide and iodide, proportional to the temperature, and the true specific heat is perfectly constant. At higher temperatures up to the point of fusion, the quantity of heat and the true specific heat of lead iodide and bromide, and especially of silver and lead chlorides, increase in a greater ratio than that of the temperature, the phenomenon being the more marked the nearer the temperature to the point of fusion. The melting of such substances does not seem to consist of a sudden transformation from the solid to the liquid state, but rather of a gradual softening process. Thus, then, the latent heat of fusion cannot be referred to a definite temperature point, but is distributed over a wider interval of temperature. The concept of the latent heat of fusion is thus relative, and requires not only determinations of the specific heats of the substances in the solid state, but also of the maximum and constant specific heats at higher temperatures.

The more important determinations are collected in the following table:—

	Mean specific heat before softening.	Mean specific heat above melting point.	Melting point.	Latent heat of fusion.
Silver chloride..	0.0980	—	about 490°	—
Lead chloride..	0.0710	0.1035	485	20.9
Lead bromide..	0.0534	—	490	12.34
Lead iodide ....	0.0430	0.0645	373	11.5

V. H. V.

**Absorption of Radiant Heat by Carbonic Anhydride.** By J. E. KEELER (*Amer. J. Sci.* [3], 28, 190).—The author's experiments show that the luminous rays of the spectrum are not appreciably absorbed by a column of carbonic anhydride 3.4 metres in length, although the same rays are strongly absorbed by the column of atmospheric air containing the same amount of carbonic anhydride. As the decreasing wave-lengths of the radiations approach a certain limit in the invisible part of the spectrum, the absorption by the gas becomes greater, corresponding to the production of a broad absorption band beyond the red. The absorption by carbonic anhydride is strongly selective, the radiations from a Bunsen flame, for example, being very largely absorbed. The author believes that the total absorptive power of the atmosphere is essentially due not to carbonic anhydride, but to some other agent.

R. R.

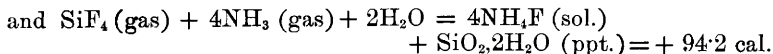
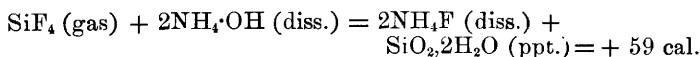
**Thermochemistry of Ammonium Fluosilicates.** By C. TRUCHOT (*Compt. rend.*, 100, 794—797).—Ammonium fluosilicate can be obtained by passing silicon tetrafluoride into a solution of ammonium fluoride. The following result was obtained:—



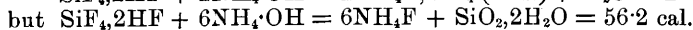
for the heat of solution of ammonium fluosilicates 8.4 cal. at 7°; hence from these values and that of the solution of ammonium fluoride (3.0 cal.) then—



By the action of ammonia on silicon tetrafluoride there are produced ammonium fluoride and silicic acid. The thermic results are as follows:—



Ammonia behaves towards fluosilicic acid as the alkaline hydroxides, in forming the salt of the acid. The changes can be represented thus (1 equivalent in the litre):—



Thus if to 1 equivalent of hydrofluosilicic acid 0—3 equivalents of ammonia are added, the quantity of heat evolved increases propor-

tionally to the ammonia added up to 1 equivalent, then it is proportional to the ammonia added in excess. These phenomena would be represented graphically by two straight lines meeting at an angle, the summit of which corresponds with 1 equivalent of ammonia. By the electrolysis of an aqueous solution of ammonium fluosilicate 79·2 cal. were evolved, a result in accordance with the supposition that the salt is at first decomposed into its constituents, ammonium and silicon fluorides, and that the latter is decomposed by the water present.

V. H. V.

**Formation of Glyoxal Ammonium Hydrogen Sulphite.** By DE FORCRAND (*Compt. rend.*, 100, 748—751).—In the formation of glyoxal ammonium hydrogen sulphite by the direct addition of its constituents according to the equation  $C_2H_2O_2 + 2(NH_4HSO_3)$  diss. =  $C_2H_3O_2, 2NH_4HSO_3$ , diss., 14·22 cal. are evolved. This value is approximately equal to the heat evolved in the formation of the corresponding potassium compound (14·96 cal.), but rather greater than those of the sodium (11·03 cal.), and barium (10·69 cal.) compounds. The results may also be compared in another way, viz., as the heat of neutralisation of glyoxal sulphurous acid by the alkalis in question. The following numbers are given:—

	$Na_2O$ (diss.)	$K_2O$ (diss.)	$BaO$ (diss.)	$(NH_4)_2O$ (diss.)
$C_2H_2O_2, 2H_2SO_3 \dots$	33·1	36·92	34·56	32·54

V. H. V.

**Bromine Substitutions.** By BERTHELOT and WERNER (*Compt. rend.*, 100, 688—692).—This paper is a continuation of the thermochemical investigation of the substitution of bromine for hydrogen in the phenols (Abstr., 1884, 883). The mean results were as follows:—

	Develops
<i>Orcinol</i> , $C_7H_8O_2$ (diss.) + $3Br_2$ (diss.) = $3HBr$ (diss.) + $C_7H_5Br_3O_2$ (solid) .....	61·9 cal.
<i>Phloroglucol</i> , $C_6H_6O_3$ (diss.) + $3Br_2$ (diss.) = $3HBr$ (diss.) + $C_6H_3Br_3O_3$ (solid) .....	61·82 „
<i>Pyrogallol</i> , $C_6H_6O_3$ (diss.) + $Br_2$ (diss.) = $2HBr$ (diss.) + $C_6H_5BrO_3$ .....	22·42 „
„ $C_6H_6O_3$ (diss.) + $2Br_2$ (diss.) = $2HBr$ (diss.) + $C_6H_4Br_2O_3$ .....	43·81 „
„ $C_6H_6O_3$ (diss.) + $3Br_2$ (diss.) = $3HBr$ (diss.) + $C_6H_3Br_3O_3$ .....	61·17 „
<i>Resorcinol</i> , $C_6H_6O_2$ (diss.) + $3Br_2$ (diss.) = $3HBr$ (diss.) + $C_6H_3Br_3O_2$ (solid) .....	63·16 „
<i>Catechol</i> , $C_6H_6O_2$ (diss.) + $Br_2$ (diss.) = $HBr$ (diss.) + $C_6H_5BrO_2$ .....	14·79 „
„ $C_6H_6O_2$ (diss.) + $2Br_2$ (diss.) = $2HBr$ (diss.) + $C_6H_4Br_2O_2$ .....	31·69 „
„ $C_6H_6O_2$ (diss.) + $3Br_2$ (diss.) = $3HBr$ (diss.) + $C_6H_3Br_3O_2$ .....	43·6 „

Thus in the cases of pyrogallol and catechol, the quantity of heat evolved is very nearly proportional to the quantity of bromine entering into the reaction, although with quinol no such relation exists.

Quinol, $C_6H_6O_2$ (diss.) + $Br_2$ (diss.) = $HBr$ (diss.) + $C_6H_5BrO_2$ .....	12.21 cal.
„ $C_6H_6O_2$ (diss.) + $2Br_2$ (diss.) = $2HBr$ (diss.) + $C_6H_4Br_2O_2$ .....	13.6 „
„ $C_6H_6O_2$ (diss.) + $3Br_2$ (diss.) = $3HBr$ (diss.) + $C_6H_3Br_3O_2$ .....	14.21 „
„ $C_6H_6O_2$ (diss.) + $4Br_2$ (diss.) = $4HBr$ (diss.) + $C_6H_2Br_4O_2$ .....	14.59 „

The result is due to the formation of quinone by the oxidation of the quinol which complicates the above reactions. V. H. V.

**Isomerism in the Benzene Series : Heat of Neutralisation of Polyhydric Phenols.** By BERTHELOT and WERNER (*Compt. rend.*, 100, 586—591).—*Resorcinol*.—Heat of solution in 400  $H_2O$  at about  $10^\circ$  — 3.243 cal.; heat of neutralisation—

$C_6H_6O_2$ (1 eq. = 3 lit.) + $NaHO$ (2 lit.) develops	+ 8.226 cal.
„ „ + $2NaHO$ „ „	+ 7.359 „
„ „ + $3NaHO$ „ „	+ 0.705 „
<hr/>	
	+ 16.290 cal.

These numbers show that resorcinol behaves as a dihydric phenol, having twice the heat of neutralisation of ordinary phenol (+ 7.9). The fact that complete neutralisation only takes place in presence of an excess of alkali, indicates that the dibasic compound is partially dissociated by water.

*Orcinol*.—Heat of solution, anhydrous, —2.366; heat of solution of the hydrate,  $C_7H_8O_2 \cdot H_2O$ , —5.426; heat of formation of the hydrate, from orcinol and liquid water, +3.06; from solid water, +1.63. Solutions of anhydrous orcinol and of orcinol hydrate are identical, and develop the same quantity of heat when neutralised with an alkali. The behaviour of orcinol on neutralisation is exactly similar to that of its homologue resorcinol.

*Quinol*.—Heat of solution —4.18 cal.; heat of neutralisation—

$C_6H_6O_2$ (6 lit.) + $NaHO$ (2 lit.) develops	+ 8.001	} + 15.56
„ „ + $2NaHO$ „ „	+ 6.361	
„ „ + $3NaHO$ „ „	+ 1.199	
„ „ + $4NaHO$ „ „	+ 0.000	

Quinol behaves as a dihydric phenol, and has practically the same heat of neutralisation as resorcinol, but the dissociation of the dibasic compound is somewhat more marked.

*Catechol*.—Heat of solution —2.92; heat of neutralisation—

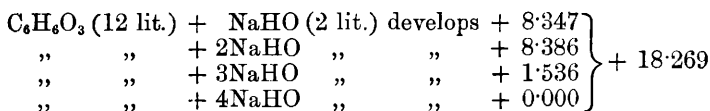
$C_6H_6O_2$ (6 lit.) + $NaHO$ (2 lit.) develops	+ 6.257	} + 8.267
„ „ + $2NaHO$ „ „	+ 1.405	
„ „ + $3NaHO$ „ „	+ 0.605	



Catechol, unlike its two isomerides, does not behave as a dihydric phenol, but has only the same heat of neutralisation as ordinary phenol. The development of heat is progressive, and this indicates that even the monobasic compound is dissociated by water. The dibasic derivative does not exist in presence of the quantities of water employed, probably because it is decomposed in the same manner as an alcoholate. Catechol would therefore seem to behave as a phenol alcohol, and the difference between it and its isomerides is doubtless connected with the fact that in catechol the substitution of the two OH-groups has taken place in the same acetylene-group, whilst in the other two compounds substitution has taken place in different acetylene-groups.

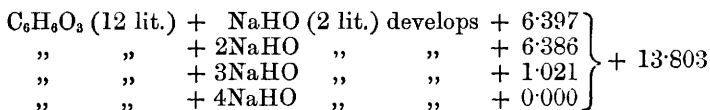
*Quinone*.—Heat of solution  $-4.23$  cal. When mixed with an alkali, quinone is not simply neutralised, but undergoes a more complex change, becoming dark-coloured even in an atmosphere of nitrogen.

*Phloroglucol*.—Heat of solution, anhydrous,  $-1.64$  cal.; of the hydrate,  $C_6H_6O_3 \cdot 2H_2O$ ,  $-6.67$  cal.; heat of formation of the hydrate, from liquid water,  $+2.513 \times 2$ ; from solid water,  $+1.08 \times 2$ ; heat of neutralisation—



It follows that two of the hydroxyl-groups in phloroglucol have a phenolic function, whilst the third has an alcoholic function and its metallic derivative is dissociated in presence of water.

*Pyrogallol*.—Heat of solution  $-3.713$ ; heat of neutralisation—



Pyrogallol, like phloroglucol, behaves as a dihydric phenol and an alcohol, but the quantities of heat developed are somewhat smaller. Only one of the trihydroxy-benzenes can have the three hydroxyl-groups in non-contiguous positions (1 : 3 : 5), and this derivative, which is at present unknown, may be expected to behave as a trihydric phenol, after the manner of the dihydric phenols, resorcinol and quinol. The other trihydroxy-derivatives, phloroglucol and pyrogallol, must have at least two hydroxyl-groups in contiguous positions (1 : 2 : 3 and 1 : 2 : 4), and hence behave after the manner of pyrocatechol, having the properties of a dihydric phenol and an alcohol. It is possible that the most feebly acid derivative, pyrogallol, has the hydroxyl-groups in the three contiguous positions (1 : 2 : 3).

C. H. B.

**Influence of Change from Liquid to Solid State on Vapour Pressures.** By W. RAMSAY and S. YOUNG (*Proc. Roy. Soc.*, **36**, 499—500).—The object of this research is to demonstrate experi-

mentally that the pressure exerted by the vapour of a solid substance at a given temperature is less than that exerted by the same substance in the liquid form at the same temperature. Regnault came to an opposite conclusion from his experiments, and his conclusion is generally accepted. Four substances, camphor, benzene, acetic acid, and water, as representing very different chemical types, were selected for the experiments, and it was invariably found that the vapour pressure of the solid is less than that of the liquid at the same temperature; the difference between the latter are calculable from thermal data in cases where these are known. The method of investigation, which is to be described in a future communication, presents important advantages over the barometric method, the results from which are always capricious.

V. H. V.

**Decomposition of Salts by Water.** By H. LE CHATELIER (*Compt. rend.*, **100**, 737—740).—Former experiments on the conditions of chemical equilibrium led the author to propound the following propositions:—(I.) The quantity of free acid required to prevent the decomposition of a salt by water increases indefinitely with the proportion of salt contained in solution. (II.) The decomposition of a dissolved salt increases or decreases by rise of temperature according as this decomposition is an endo- or exo-thermic change. Although these propositions are in direct opposition to commonly received views, they are further exemplified in this paper by a study of the decomposition of antimony trichloride and of mercuric sulphate by water, the former constituting an endothermic, the latter an exothermic change. The results obtained were analogous to those of Schloesing and Engel on the decomposition of calcium and magnesium hydrogen carbonates with water. Thus if A represent the quantity of free acid, and S that of the mercuric sulphate, the relation between them may be expressed by the equation  $A^{1.58} = 4.7S$ . In the case of antimony trichloride the equation takes the form of  $A^{0.8} = k'S$  or  $A^8 = k''S$ , according as the oxychloride,  $Sb_2O_5Cl$ , is precipitated from dilute, or  $SbO_2Cl$  from concentrated solutions.

V. H. V.

### **Solubility of Carbon Bisulphide and Chloroform in Water.**

By G. CHANCEL and F. PARMENTIER (*Compt. rend.*, **100**, 773—776).—The solubility of carbon bisulphide in water decreases with the temperature; at 0° 1 litre of water dissolves 2.04 grams of carbon bisulphide, but at 49° only 0.14 gram; thus, as regards its solubility, it resembles those gases which dissolve in, but form no chemical combination with water.

The solubility of chloroform decreases with the temperature from 0° to 30°, but from 30° to 55° it increases; thus the temperature of 30° seems to be the point of minimum solubility. These results were further exemplified by determinations of the density of the resultant solutions, the temperature of 30° corresponding with the point of minimum density; the values obtained were greater than the mean densities of corresponding proportions of water and chloroform, there is thus a contraction in the process of solution. It is further observed that an aqueous solution of chloroform saturated at 4° is rendered

turbid on warming by precipitation of chloroform, and conversely a solution saturated at 59° is rendered turbid on cooling, but a solution saturated at 30° remains unaltered. Determinations are also given of the density of chloroform at various temperatures, from 0 to 35°, the mean coefficient of expansion deduced from these experiments is 0.00129, a value slightly higher than that found by Pierre.

V. H. V.

**Difference between Crystalline and Anisotropic Structures.** By V. v. EBNER (*Monatsh. Chem.*, **6**, 48—62).

**Oxidation and Reduction.** By LEDEBUR (*Chem. Centr.*, 1884, 99).

**Apparatus for Chemical Laboratories.** By J. WALTER (*J. pr. Chem.* [2], **31**, 116—119).—A description of a hand-regulator for the electric light, as used in projecting spectra on the screen.

P. P. B.

**Apparatus for Continuous Percolation with Boiling Liquids.** By W. W. WILL (*Pharm. J. Trans.* [3], **15**, 363).

**Apparatus for Filtering in a Vacuum or in a Current of Gas.** By F. ALLIHN (*Zeit. Anal. Chem.*, **23**, 517—518).

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## Inorganic Chemistry.

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### Density and Atomic Volumes of Oxygen and Hydrogen.

By E. H. AMAGAT (*Compt. rend.*, **100**, 633—635).—The author has constructed apparatus by which he is able to subject gases to a pressure of about 400 atmos. He has several times reduced oxygen to one nine-hundredth part of its original volume, and under these conditions the density of the oxygen is considerably higher than that of water. Under the highest pressure yet obtained, the density of the oxygen was higher than 1.25, the surrounding temperature being 17°. It is evident, therefore, that unity is not the limiting density of oxygen. The limiting density of hydrogen deduced from the author's experiments is 0.12, and it follows that on L. Meyer's curve the summit of the ordinate representing the atomic volume of hydrogen, will fall on the regular prolongation of the curve passing through the summits of the corresponding ordinates for lithium, sodium, and potassium.

C. H. B.

**Modification of Tissander's Apparatus for the Preparation of Hydrogen.** By C. CLOEZ (*Bull. Soc. Chm.*, **43**, 102—106).

**Decomposition of Aqueous Solutions of Hypochlorous Acid and of Chlorine in Sunlight.** By A. POPPER (*Annalen*, **227**,

161—180).—The results of the investigation lead to the following conclusions:—Chlorine-water, on exposure to sunlight, is probably converted into hydrochloric and chloric acids, whilst oxygen is given off; perchloric acid is not formed; the question as to the formation of hypochlorous acid is left unsettled.

When an aqueous solution of hypochlorous acid is exposed to sunlight, it yields chloric acid, oxygen, chlorine, and small quantities of perchloric acid.

A. J. G.

**Action of Bromine on Chlorides.** By BERTHELOT (*Compt. rend.*, **100**, 761—767).—Concentrated solutions of hydrochloric acid and of metallic chlorides absorb considerable quantities of bromine with evolution of heat, thus pointing to the formation of additive compounds, the perbromides of the chlorides. The resultant solutions slowly give up bromine when a current of air is passed through them. Their formation is always accompanied by the displacement of a small quantity of the chlorine by bromine, attended possibly by the generation of chlorobromides. In this paper, the exothermic reactions of bromine with hydrochloric acid and the chlorides of barium, strontium, and calcium, are studied.

V. H. V.

**Thiophosphoric Acid.** By C. KUBIERSCHKY (*J. pr. Chem.* [2], **31**, 93—111).—*Monothiophosphoric Acid*.—*Sodium monothiophosphate*,  $\text{Na}_3\text{PSO}_3 + 12\text{H}_2\text{O}$ , is obtained by adding powdered phosphorus pentasulphide to a moderately concentrated solution of sodium hydroxide, in the proportion of  $6\text{NaHO}$  to  $\text{P}_2\text{S}_5$ .

The mixture formed by this reaction is next treated with alcohol, and in this way a precipitate of thiophosphates is obtained; the precipitated thiophosphates are dissolved in water and the solution heated at  $90^\circ$  for some time, in order to decompose the dithiophosphate into monothiophosphate; from this solution, on cooling, the latter separates out in white six-sided tablets, melting at  $60^\circ$ . This salt is identical with that obtained by Würtz by the action of phosphorus thiochloride on sodium hydroxide (*Ann. Chim. Phys.* [3], **20**, 443). *Potassium* and *ammonium monothiophosphates* are produced in a manner similar to the above, but have only been obtained in solution. *Magnesium monothiophosphate*,  $\text{Mg}_3\text{P}_2\text{S}_2\text{O}_6 + 20\text{H}_2\text{O}$ , is obtained as a white crystalline precipitate on adding a solution of sodium monothiophosphate to a solution of magnesium sulphate. *Magnesium ammonium monothiophosphate*,  $\text{MgNH}_4\text{PSO}_3 + 9\text{H}_2\text{O}$ , is obtained as a white crystalline precipitate in a manner similar to the magnesium salt.

*Dithiophosphoric Acid*.—*Sodium dithiophosphate*,  $\text{Na}_3\text{PS}_2\text{O}_2 + 11\text{H}_2\text{O}$ , is obtained by dissolving in water the mixture of thiophosphates, resulting from the action of phosphorus pentasulphide on sodium hydroxide, and heating the solution at  $50$ — $55^\circ$ , until all trithiophosphate has been destroyed, as shown by a drop of the solution giving a green instead of a yellow or brown coloration with a solution of cobalt sulphate. The solution is now cooled, as further heating converts the dithiophosphate into the monothiophosphate, and alcohol is added; a precipitate of almost pure sodium dithiophosphate is then formed,

which may be purified by crystallisation from water. It forms colourless six-sided crystals, melting at  $45-46^{\circ}$ ; it decomposes into monothio-phosphate or phosphate and sulphur, at temperatures a little above the ordinary. *Potassium dithiophosphate* has only been obtained in solution. *Ammonium dithiophosphate*,  $(\text{NH}_4)_3\text{PS}_2\text{O}_2 + 2\text{H}_2\text{O}$ , is prepared by the action of ammonia solution on phosphorus pentasulphide; it crystallises in fine needles which effloresce, and at the same time decompose with separation of sulphur. *Barium dithiophosphate*,  $\text{Ba}_3\text{P}_2\text{S}_4\text{O}_4 + 8\text{H}_2\text{O}$ , is obtained as a white precipitate on adding sodium dithiophosphate to a solution of barium chloride. *Calcium and magnesium dithiophosphates* are formed by adding phosphorus pentasulphide to solutions of the hydrosulphides of these metals; they are both soluble unstable compounds. *Magnesium ammonium dithiophosphate*,  $\text{MgNH}_4\text{PS}_2\text{O}_2 + 6\text{H}_2\text{O}$ , is obtained in the same manner as the monothio-phosphate, to which it exhibits the greatest resemblance.

*Trithiophosphoric Acid*.—The author has not succeeded in isolating *sodium trithiophosphate*, but it is apparently formed together with the dithiophosphate when phosphorus pentasulphide is made to react with a solution of sodium hydrosulphide at  $20^{\circ}$ .

*Reactions of the Thiophosphates*.—Acids decompose all thiophosphates; hydrogen sulphide is evolved, and, in some cases, sulphur separates. Monothio-phosphates give white precipitates with calcium, barium, and strontium salts, the dithiophosphates with barium and strontium, and the trithiophosphates with barium salts only. All thiophosphates yield precipitates with cadmium, copper, silver, and mercurous salts, which decompose after a time, forming the sulphides of the metals. With a dithiophosphate, manganese sulphate gives a green coloration, which becomes darker on shaking; a further addition of manganese sulphate gives a dark green precipitate, which gradually becomes white, but on shaking changes back to green. Ferrous salts give a dirty greyish-green precipitate with monothio-phosphates. Ferric salts give red colorations with all thiophosphates, from which solutions, on boiling, ferrous sulphide separates out. An excess of ferric chloride gives a precipitate with monothio-phosphates only, which, on continued boiling, is decomposed with the production of iron phosphate and sulphuretted hydrogen. A solution of a thio-phosphate containing a small quantity of an alkaline sulphide gives an intense green coloration with ferric chloride. Cobalt sulphate gives a blue precipitate with a monothio-phosphate soluble in excess of the latter to a blue solution; the dithiophosphates give dirty green precipitates, soluble in excess of the thiophosphate to green solutions; the trithiophosphates give a red to a brown coloration. In each case, boiling produces a precipitate of cobalt sulphide. Nickel sulphate in excess gives a light green precipitate with monothio-phosphates, and a dirty blue precipitate with a dithiophosphate. Many of these coloured solutions produced as above described, exhibit characteristic absorption-spectra. Nitric acid decomposes all thiophosphates with a precipitation of sulphur; potassium permanganate, dichromate, and ferri-cyanide, are reduced by thiophosphates, sulphur separating out in each case. Monothio-phosphates decolorise iodine solutions with an immediate precipitation of sulphur, whereas in the case of the di- and

tri-thiophosphates the separation of sulphur takes place only after some time or on boiling.

P. P. B.

**Reduction of Arsenic Acid Solutions by means of Sulphurous Anhydride.** By L. W. McCAY (*Chem. News*, **51**, 122).—Arsenic acid is completely reduced to arsenious acid if heated for one hour in closed vessels with an excess of a solution of sulphurous anhydride in water.

D. A. L.

**Apparatus for Preparing Pure Carbonic Anhydride.** By A. MUENCKE (*Chem. Centr.*, 1884, 179—180).

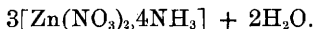
**Solubility of Lithium Carbonate.** By BEVADE (*Bull. Soc. Chim.*, **43**, 123).—100 parts of water at 0° dissolve 1.539 parts of  $\text{Li}_2\text{CO}_3$ ; at 10°, 1.406 parts; at 20°, 1.329 parts; at 50°, 1.181 parts; at 75°, 0.866 part; at 100°, 0.728 part. After boiling for 15 minutes, 100 parts of water at 102° contain 0.796 part of lithium carbonate, and after boiling for half an hour 0.955 part. The solubility of lithium carbonate therefore diminishes with the rise of temperature up to 100°, and afterwards, by continued boiling, the solubility increases, this increase being due to the formation of a basic salt which is less soluble in cold than hot water.

A. P.

**Occlusion of Hydrogen by Zinc-dust, and the Meteoric Iron of Lenarto.** By G. WILLIAMS (*Chem. News*, **51**, 146—147).—The author finds that the commercial zinc-dust employed in the experiments described in a previous communication (this vol., p. 369) contained 39 times its volume of hydrogen. As the metal had not been exposed to an atmosphere of hydrogen, he concludes that this is derived originally from water. This conclusion finds support in the fact that the temperature rises considerably when zinc-dust is moistened. The author extends this view, and now attributes the hydrogen in the meteoric iron of Lenarto to the same source.

D. A. L.

**Basic and Ammoniacal Nitrates.** By J. ANDRÉ (*Compt. rend.*, **100**, 639—641).—If a current of ammonia gas is passed into a solution of zinc nitrate until the precipitate, which first forms, redissolves, and the liquid is then evaporated at a gentle heat and allowed to cool, it deposits deliquescent crystals of the ammonio-nitrate—



The same compound is obtained as a bulky crystalline precipitate by avoiding a rise of temperature, but passing the gas into the zinc nitrate solution for a long time. When exposed to the air, the ammonio-nitrate gives off ammonia, and this gas is also evolved on heating. It is very soluble in a small quantity of water, but is decomposed by a larger quantity, especially if heated, with precipitation of zinc oxide. In this respect it resembles ammonio-zinc sulphate, but differs from the ammoniacal chlorides and bromides. A warm solution of ammonium nitrate slowly dissolves zinc oxide, and the filtered solution, when cooled, deposits the compound  $3\text{N}_2\text{O}_5, 13\text{ZnO}, 4\text{NH}_3 + 18\text{H}_2\text{O}$  in lamellæ

grouped in hemispherical masses. This compound does not alter when exposed to air, and is insoluble in cold water, but is decomposed by hot water with separation of zinc oxide. If the 4 mols. of  $\text{NH}_3$  are regarded as replacing  $2\text{ZnO}$ , the constitution of this compound corresponds with  $5\text{ZnO}, \text{N}_2\text{O}_5$ , a basic nitrate which has not yet been prepared.

When zinc oxide is heated with a solution of ammonium sulphate, the only product is the well-known double zinc-ammonium sulphate. If litharge is dissolved in a hot solution of ammonium nitrate in an equal weight of water, and the liquid filtered and allowed to cool, it deposits small crystals of the basic nitrate,  $2\text{PbO}, \text{N}_2\text{O}_5 + 2\text{H}_2\text{O}$ , free from ammonia. If the mother-liquor is poured into a large quantity of cold water, the same compound is obtained as a white amorphous precipitate. The same basic nitrate was prepared by Chevreul by boiling a solution of the normal nitrate with lead oxide, and by Pelouze by heating together lead nitrate and carbonate.

If the mother-liquor, instead of being poured into cold water, is heated with water in sealed tubes at  $225^\circ$  for about five hours, the compound  $\text{N}_2\text{O}_5, 3\text{PbO} + 4\text{H}_2\text{O}$  separates on cooling in nacreous lamellæ, which are free from ammonia, and tarnish very rapidly when exposed to the air. A compound of the same composition was obtained by Berzelius by adding a slight excess of ammonia to a solution of normal lead nitrate.

C. H. B.

**Action of Hydrogen Peroxide on Cerium and Thorium Oxides.** By L. DE BOISBAUDRAN (*Compt. rend.*, 100, 605—607).—When a solution of cerous sulphate is mixed with a slight excess of ammonia, and hydrogen peroxide is added, a precipitate of cerium trioxide,  $\text{CeO}_3$ , is obtained. The orange-red precipitates formed when a solution of cerium acetate is treated with hydrogen peroxide do not contain such a high proportion of oxygen. Cerium compounds are sometimes recognised by mixing the solution with an alkaline acetate, adding hydrogen peroxide, and heating gently, when an orange-red precipitate is formed. In the case of cerous salts, the precipitate not unfrequently remains white, or at most becomes pale yellow. This precipitate should be moistened with ammonia, and again treated with hydrogen peroxide, when the orange-red colour will be produced. The white precipitate formed by hydrogen peroxide in solutions of cerous acetate does not appear to be more highly oxidised than  $\text{Ce}_2\text{O}_3$ , but it is difficult to explain the production of this compound under these conditions.

When a solution of thorium acetate is heated with hydrogen peroxide, a white precipitate of a peroxide is produced, but by treating a solution of a thorium salt with ammonia and hydrogen peroxide in the cold, a still higher oxide,  $\text{Th}_2\text{O}_7$ , is obtained.

C. H. B.

**Action of Hydrogen Peroxide upon the Rare Earths.** By P. T. CLÈVE (*Bull. Soc. Chim.*, 43, 53—58).—The oxides of yttrium, lanthanum, samarium, and didymium—all of them sesquioxides—when treated with hydrogen peroxide, yield peroxides of the general formula  $\text{R}_4\text{O}_9$ , the dioxides of zirconium and cerium give peroxides



having the composition  $\text{RO}_3$ . The oxide of thorium, however, which belongs to the same group, gives a peroxide of the formula  $\text{Th}_2\text{O}_7$ .

H. B.

**Samarium Compounds.** By P. T. CLÈVE (*Bull. Soc. Chim.*, **43**, 162—172).—Samarium is separated from the closely allied metals in the form of the hydroxide, by the fractional precipitation of the dilute solution of the nitrates with ammonia, the samarium being contained in the first fractions. Samarium has not yet been isolated. The determination of the atomic weight by synthesis of the sulphate from the oxide gives as a mean 150.021. *Samarium oxide*,  $\text{Sm}_2\text{O}_3$ , is an infusible yellowish-white powder, having a density of 8.347. It dissolves easily in acids, forming yellow salts. It is neither reduced by hydrogen nor further oxidised by oxygen, even at a red heat. *Samarium hydroxide*, obtained by precipitation, forms, when dried, resinous looking, yellowish fragments. It absorbs carbonic anhydride. The aqueous solutions of samarium salts have a sweet but very astringent taste. On the addition of hydrogen sulphide, samarium hydroxide is precipitated. *Samarium fluoride*,  $2\text{SmF}_3 + \text{H}_2\text{O}$ , is a gelatinous and transparent precipitate, becoming pulverulent on heating. *Samarium chloride*,  $\text{SmCl}_3 + 6\text{H}_2\text{O}$ , forms large deliquescent crystals, sp. gr. 2.383. *Samarium oxychloride*,  $\text{SmOCl}$ , obtained by heating the oxide in chlorine, is a white powder of sp. gr. 7.017. *Samarium bromide*,  $\text{SmBr}_3 + 6\text{H}_2\text{O}$ , is obtained in large tabular deliquescent crystals of sp. gr. 2.971. *Samarium platinochloride*,  $\text{SmCl}_3, \text{PtCl}_4 + 10\frac{1}{2}\text{H}_2\text{O}$ , is obtained in orange-coloured deliquescent crystals of sp. gr. 2.712. The *aurochloride*,  $\text{SmAuCl}_6 + 10\text{H}_2\text{O}$ , is obtained in intensely yellow deliquescent rhombic tables of sp. gr. 2.742. The *aurobromide*,  $\text{SmAuBr}_6 + 10\text{H}_2\text{O}$ , crystallises in thick deliquescent dark brown tablets of sp. gr. 3.39. The *ferrocyanide*,  $\text{SmKFeCy}_6 + n\text{H}_2\text{O}$ , is obtained as a dirty yellow precipitate. The *platinocyanide*,  $\text{Sm}_2\text{Pt}_2\text{Cy}_{12} + 18\text{H}_2\text{O}$ , crystallises in yellow prisms with blue lustre, sp. gr. 2.744. The *sulphocyanate*,  $\text{Sm}(\text{CNS})_3 + 6\text{H}_2\text{O}$ , crystallises in deliquescent needles; this compound combines with mercuric cyanide to form a double salt,  $\text{Sm}(\text{CNS})_3, 3\text{HgCy}_2 + 12\text{H}_2\text{O}$ , which crystallises in colourless needles of sp. gr. 2.745. *Samarium nitrate*,  $\text{Sm}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$ , crystallises in flattened and radiating prisms, sp. gr. 2.375. The *iodate*,  $\text{Sm}(\text{IO}_3)_3 + 6\text{H}_2\text{O}$ , is an amorphous precipitate, obtained on the addition of iodic acid to solutions of samarium salts. The *periodate*,  $\text{SmIO}_5 + 4\text{H}_2\text{O}$ , is a crystalline precipitate, obtained on adding periodic acid to solutions of samarium salts; its sp. gr. = 3.793.

The anhydrous *sulphate*,  $\text{Sm}_2(\text{SO}_4)_3$ , is a yellowish-white powder of sp. gr. 3.898. The crystallised *sulphate*,  $\text{Sm}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$ , has a sp. gr. of 2.930. Samarium potassium sulphate,  $2\text{Sm}_2(\text{SO}_4)_3, 9\text{K}_2\text{SO}_4 + 3\text{H}_2\text{O}$ , is obtained by adding excess of potassium sulphate to a solution of samarium acetate; it is a white powder, only slightly soluble in a saturated solution of potassium sulphate. Samarium sodium sulphate,  $\text{SmNa}(\text{SO}_4)_2 + \text{H}_2\text{O}$  (?), is obtained as a slightly crystalline precipitate on mixing solutions of samarium and sodium sulphates. Samarium ammonium sulphate,  $\text{SmNH}_4(\text{SO}_4)_2 + 4\text{H}_2\text{O}$ , is obtained in small yellowish-white crystals, which are but slightly soluble; sp. gr. 2.675. The anhydrous salt has been prepared, and

has a density of 3.191. Anhydrous *samarium selenate*,  $\text{Sm}_2(\text{SeO}_4)_3$ , forms a yellowish powder of sp. gr. 4.077. The crystalline selenate,  $\text{Sm}_2(\text{SeO}_4)_3 + 8\text{H}_2\text{O}$ , is obtained in small yellow crystals of sp. gr. 3.327; a second crystalline selenate has also been obtained,  $\text{Sm}_2(\text{SeO}_4)_3 + 12\text{H}_2\text{O}$ ; it crystallises in brilliant prisms at about  $10^\circ$ , which alter rapidly in the air; sp. gr. 3.009. *Samarium potassium selenate*,  $\text{SmK}(\text{SeO}_4)_2 + 3\text{H}_2\text{O}$ , crystallises in small brilliant prisms of a topaz-yellow colour, easily soluble in water; sp. gr. 3.541. The anhydrous compound has a density of 3.956. *Samarium ammonium selenate*,  $\text{SmNH}_4(\text{SeO}_4)_2 + 3\text{H}_2\text{O}$ , is obtained in serrated crystals easily soluble in water; sp. gr. 3.274. The anhydrous compound has a density of 3.805. Samarium does not form a double selenate with sodium. *Samarium sulphite*,  $\text{Sm}_2(\text{SO}_3)_3 \cdot 3\text{H}_2\text{O}$ , is obtained by dissolving the oxide in sulphurous acid. Samarium forms two *selenites*—1st, a basic compound,  $3\text{Sm}_2\text{O}_3 \cdot 8\text{SeO}_2 + 7\text{H}_2\text{O}$ , which is obtained as an amorphous gelatinous precipitate on adding neutral sodium selenite to a solution of samarium sulphate. 2nd, a compound having the constitution  $\text{Sm}_2\text{O}_3(\text{SeO}_2)_4 + 5\text{H}_2\text{O}$ , is obtained as a heavy crystalline powder on adding a solution of selenious acid to samarium acetate.

*Samarium carbonate*,  $\text{Sm}_2(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ , is obtained by passing carbonic anhydride through water containing samarium hydroxide in suspension. *Samarium potassium carbonate*,  $\text{SmK}(\text{CO}_3)_2 + 6\text{H}_2\text{O}$ , is obtained in brilliant flattened needles by precipitating samarium nitrate with potassium carbonate. *Samarium ammonium carbonate*,  $\text{SmNH}_4(\text{CO}_3)_2 + 2\text{H}_2\text{O}$ , is obtained as a compact powder. *Samarium sodium carbonate*,  $\text{SmNa}(\text{CO}_3)_2 + 8\text{H}_2\text{O}$ , is a crystalline precipitate.

*Anhydrous samarium orthophosphate*,  $\text{SmPO}_4$ , is obtained by saturating fused sodium metaphosphate with samarium oxide; it is insoluble in nitric acid, and has a sp. gr. of 5.827. *Hydrated samarium orthophosphate*,  $\text{SmPO}_4 + 2\text{H}_2\text{O}$  (?), is an amorphous white precipitate. The *pyrophosphate*,  $\text{SmHP}_2\text{O}_7 + 3\frac{1}{2}\text{H}_2\text{O}$ , is obtained as a hard crystalline crust on dissolving samarium hydroxide in pyrophosphoric acid. The *metaphosphate*,  $\text{Sm}_2\text{O}_3(\text{P}_2\text{O}_5)_5$ , is formed on adding anhydrous samarium sulphate to metaphosphoric acid heated to redness, and is obtained as a powder of brilliant well-formed microscopic crystals of sp. gr. 3.487. Two *vanadates* of samarium have been obtained, a red salt,  $\text{Sm}_2\text{O}_3(\text{V}_2\text{O}_5)_5 + 28\text{H}_2\text{O}$ , of sp. gr. 2.524, and a yellow compound,  $\text{Sm}_2\text{O}_3(\text{V}_2\text{O}_5)_5 \cdot 24\text{H}_2\text{O}$ , of sp. gr. 2.524. *Samarium borate*,  $\text{SmBO}_3$ , is obtained as micaceous, lamellar, hexagonal crystals of sp. gr. 6.048 on fusing samarium oxide with borax at a white-red heat.

The *molybdate*,  $\text{Sm}_2(\text{MoO}_4)_3$ , is obtained in adamantine crystals, coloured violet by traces of oxide of molybdenum; sp. gr. 5.95. The *metatungstate*,  $\text{Sm}_2\text{O}_3 \cdot 12\text{WO}_3 + 35\text{H}_2\text{O}$ , is obtained by the action of samarium sulphate on barium metatungstate. It is very soluble, of a pale yellow colour, and crystallises in octahedra, sp. gr. 3.994. *Samarium potassium chromate*,  $\text{SmK}(\text{CrO}_4)_2 + 3\text{H}_2\text{O}$ , is obtained as a crystalline precipitate on adding excess of samarium nitrate to neutral potassium chromate.

The formate, acetate, propionate, oxalate, succinate, tartrate, citrate, and ethyl sulphate, are also described.

A. P.

**Sodium Aluminate.** By F. M. LYTE (*Chem. News*, **51**, 109).—From experiments with commercial materials, it seems that the reaction between dilute solutions (1:5) of sodium aluminate and aluminium sulphate may be correctly represented by the equation  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 3\text{Na}_2\text{Al}_2\text{O}_4 = 3\text{Na}_2\text{SO}_4 + 4\text{Al}_2\text{H}_6\text{O}_6 + 6\text{H}_2\text{O}$ , thus giving  $\text{Na}_2\text{Al}_2\text{O}_4$  as the formula for sodium aluminate. On the other hand, concentrated solutions of the aluminate are liable to decompose with formation of sodium and aluminium hydroxides; this reaction tends to support another formula,  $\text{Na}_6\text{Al}_2\text{O}_6$ , which has been proposed for sodium aluminate.

D. A. L.

**Alloys of Indium and Gallium.** By L. DE BOISBAUDRAN (*Compt. rend.*, **100**, 701—703).—Although the alloys of aluminium with gallium are readily decomposed by water, yet the alloys of gallium with its analogue indium remain unaltered, and require aqua regia for their complete solution. The determination of their points of fusion presents some difficulty, inasmuch as they pass through an intermediate pasty condition before liquefaction. An alloy containing two atomic proportions of indium and one of gallium begins to soften at  $56^\circ$ , and is completely melted at  $75\text{--}80^\circ$ ; alloys containing one atomic proportion of indium with one, two, and four proportions of gallium respectively begin to soften at  $16.5^\circ$ ; above that point, liquefaction proceeds more rapidly than even that of gallium. These alloys are soft, and of a white colour, but acquire a bluish tint on addition of a further quantity of gallium; they are only dissolved to a very slight extent by dilute hydrochloric acid.

V. H. V.

**Method of Preparing Chromyl Chloride.** By H. MOISSAN (*Bull. Soc. Chim.*, **43**, 6).—Hydrogen chloride reacts at the ordinary temperature with chromic anhydride, or the lead, silver, barium, or alkaline chromates, producing chromyl chloride. The reaction is assisted by heat. Hydrogen chloride may be replaced by a mixture of chlorine and steam; but the reaction does not take place if dry chlorine gas is used. Hydrogen bromide and hydrogen iodide do not yield any chromium compounds under similar conditions.

A. P.

**Ammoniacal Compounds of Uranyl Chloride.** By F. F. REGELSBERGER (*Annalen*, **227**, 119—132).—When uranyl chloride is dissolved in ether, and the solution evaporated in a vacuum, a compound of the chloride with ether,  $\text{UO}_2\text{Cl}_2 \cdot 2\text{C}_4\text{H}_{10}\text{O}$ , is obtained in nodular groups of yellow needles; this could not be entirely freed from ether without the chloride also suffering decomposition.

When an ethereal solution of uranyl chloride is treated with dry ammonia gas, a voluminous flocculent yellow precipitate separates, which on drying over sulphuric acid forms a yellow amorphous powder of the formula  $\text{UO}_2(\text{NH}_3\text{Cl})_2 \cdot \text{C}_4\text{H}_{10}\text{O}$ ; by long exposure in a vacuum the ether is removed, and *uranyldiammonium dichloride*,  $\text{UO}_2(\text{NH}_3\text{Cl})_2$ , is left.

By exposure of dry uranyl dichloride or diammonium chloride to an atmosphere of ammonia, *uranyltriammonium dichloride*,  $\text{UO}_2\text{Cl}_2 \cdot 3\text{NH}_3$ , is obtained as an orange-yellow amorphous substance. It is not

decomposed on exposure to air, but loses ammonia on gentle heating. Some indications of a tetrammonium compound were obtained.

By the action of water on uranyldiammonium dichloride it suffers decomposition, in accordance with the two equations:  $\text{UO}_2(\text{NH}_3\text{Cl})_2 + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2 + 2\text{NH}_4\text{Cl}$ , and  $3\text{UO}_2(\text{NH}_3\text{Cl})_2 + 3\text{H}_2\text{O} = \text{U}_2\text{O}_7(\text{NH}_4)_2 + \text{U}_2\text{O}_2\text{Cl}_2 + 4\text{NH}_4\text{Cl}$ .

A. J. G.

**Separation of Titanium from Niobium and Zirconium.** By E. DEMARÇAY (*Compt. rend.*, **100**, 740—742).—The separation of titanium from niobium on the one hand, and from zirconium on the other, by the methods hitherto described, presents considerable difficulties. It is here proposed to separate niobic from titanic acid by the fractional precipitation of these substances with dilute potash from a hydrofluoric acid solution. No titanic acid is precipitated so long as the solution remains acid, and contains an excess of ammonium fluoride in solution. The potassium titanates and niobates, which are precipitated, are easily filtered. A similar process can be adopted to separate zirconium oxide from titanic acid. In the zirconium minerals of Expailly, the Ural, and Sweden, titanium oxide is present, as also in the natural tantalates and niobates, with the exception of ixiolite.

V. H. V.

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## Mineralogical Chemistry.

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**Analyses of Metallic Iron from Greenland.** By LORENZEN (*Jahrb. f. Min.*, 1885, 1, Ref., 206—207).—The author has examined chemically the masses of metallic iron from Greenland, described by Steenstrup (*Jahrb. f. Min.*, 1884, 2, 364—365). Analyses and descriptions are given of 15 specimens. B. H. B.

**The Composition and Properties of Coal in Relation to the Plants from which it is Derived.** By A. CARNOT (*Bull. Soc. Chim.*, 43, 61—63).—Although fossil plants of various kinds from the coal-measures of Commeny have nearly the same percentage composition, yet when subjected to destructive distillation the yields of volatile matter and coke show marked differences; this is attributed to the variations in the composition of the original plants. H. B.

**Isomorphism of Jordanite and Meneghinite.** By A. SCHMIDT (*Jahrb. f. Min.*, 1885, 1, Ref., 200—203).—Perfect isomorphism exists between jordanite ( $4\text{PbS}, \text{As}_2\text{S}_3$ ) and meneghinite ( $4\text{PbS}, \text{Sb}_2\text{S}_3$ ). The two minerals crystallise in the rhombic system, and have the same cleavage. The axial ratio of jordanite is  $a : b : c = 0.5375 : 1 : 2.0305$ , that of meneghinite is  $0.4862 : 1 : 1.8465$ . B. H. B.

**Hydrated Titanium Oxide from Diamantina.** By H. GORCEIX (*Jahrb. f. Min.*, 1885, 1, Ref., 208).—The author describes the hydrated titanium oxide with phosphoric acid and various earths, from the diamond diggings of Diamantina, in Brazil. The mineral is compact, reddish-yellow, often full of small cavities on the surface, and occurs deposited in running water. On the stream-banks, it is grey, with an earthy fracture and yellow streak. Density, 3.96. It scratches glass. The chemical analysis gave phosphoric acid, vanadic acid, alumina, oxides of cerium, didymium, and yttrium, with a small percentage of iron and calcium. B. H. B.

**Concentration of Zinc Carbonate in Dolomites.** By DIEULAFAIT (*Compt. rend.*, 815—818).—In order to explain the association of zinc with magnesium in dolomites, the author added to a solution of zinc sulphate (1) magnesium carbonate; (2) magnesium and calcium carbonate in equivalent proportions; (3) calcium carbonate. After 12 hours, the zinc was completely removed from the solution by the magnesium carbonate, only partially by the mixed carbonates, and not at all by the calcium carbonate. It follows that in the marine deposits of the dolomite the zinc contained in the sea could be precipitated together with the magnesium carbonate. The dolomites richer in zinc are of more ancient formation, produced probably at first by the trituration of the primæval rocks of the sea. V. H. V.

**New Alumina Lime Phosphate.** By A. DAMOUR (*Jahrb. f. Min.*, 1885, 1, Ref., 208).—This new mineral, which accompanies the diamonds in the province of Minas Geraës, forms yellowish-white grains, 1 to 5 mm. in diameter, and more or less transparent. It cleaves easily, and is optically uniaxial with positive double refraction;  $H. = 5$ , sp. gr. 3.26. Heated in a glass tube, it gives off water, bleaches, and becomes opaque. It is fusible with difficulty, and is insoluble in acids. The analysis gave the following results:—

$P_2O_5$ .	$Al_2O_3$ .	$CaO$ .	$H_2O$ .	Total.
14.87	50.66	17.33	16.67	99.53

corresponding with the formula  $P_2O_5, 5Al_2O_3, 3CaO + 9H_2O$ . The author suggests for the mineral the name of *Goyazite*, from the Brazilian province of Goyaz. B. H. B.

**Fairfieldite from Rabenstein.** By F. SANDBERGER (*Jahrb. f. Min.*, 1885, 1, Mem., 185).—The author has published (*Jahrb. f. Min.*, 1879, 370) a description of a new mineral from Rabenstein in Bavaria. As the mineral was white, and gave a distinct manganese reaction, the author gave it the name of *leucomanganite*. Having now obtained more material for examination, he finds that the mineral is identical with the *fairfieldite* of Brush and Dana. B. H. B.

**Manganese in Apatite.** By F. SANDBERGER (*Jahrb. f. Min.*, 1885, 1, Mem., 172). In an apatite, of density 3.169, from the pegmatite

vein at Zwiesel, the author has discovered an appreciable proportion of manganese. Analysis gave the following results:—

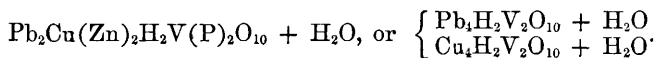
CaO.	Ca.	MnO.	P <sub>2</sub> O <sub>5</sub> .	F.	Total.
49·60	2·27	3·04	43·95	2·15	101·01

B. H. B.

**Vanadates from the Argentine Republic.** By A. DÖRING and others (*Jahrb. f. Min.*, 1885, **1**, Ref., 204—206).—The four vanadates, descloizite, vanadinite, brackebuschite, and psittacinite, occur in the western portion of the Sierra de Córdoba and in San Luis. In the latter province, at the Concepcion mine, vanadinite occurs with a mineral, which, according to Döring's researches, is identical with the psittacinite of Genth. The analysis of the psittacinite of San Luis gave the following results:—

PbO.	CuO.	ZnO.	As <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>5</sub> .	V <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	CO <sub>2</sub> .
49·25	16·29	1·08	0·29	1·14	17·23	3·41	1·93
	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O(310°).	Insoluble.	Total.			
	0·39	0·73	7·91	99·65			

From this is deduced the formula—



B. H. B.

**Mineralogical Notes.** By V. v. ZEPHAROVICH (*Jahrb. f. Min.*, 1885, **1**, Ref., 198—200).—At Kreuth in Carinthia, wulfenite crystals occur in fissures in the limestone, planted on galena or limestone. When the crystals contain lime, they are grey acute pyramids, P, 0P, P $\infty$ . Wulfenite of more recent formation also occurs in yellow tablets. The analysis of the yellow crystals (I) and of the dark crystals (II) gave the following results:—

	MoO <sub>3</sub> .	PbO.	CaO.	CuO.	$\overbrace{\text{Al}_2\text{O}_3. \text{Fe}_2\text{O}_3.}^{\quad}$	Total.
I.	39·40	57·54	1·07	0·09	1·96	100·06
II.	39·60	58·15	1·24	0·40	0·50	99·89

These figures represent isomorphic mixtures: 40PbMoO<sub>4</sub>, 3CaMoO<sub>4</sub> and 36PbMoO<sub>4</sub>, 3CaMoO<sub>4</sub> respectively.

The author also describes the following minerals: galena from the Hüttenberger Erzberg in Carinthia; pseudomorphs of anglesite after galena, from Miss in Carinthia; zoisite and pyrrhotine, from Lamprechtsberg, near Lavamünd, in Carinthia; amphibole-anthrophyllite, from Schneeberg in the Tyrol; pseudomorphs of quartz after barytes, from Koschow in North Bohemia; and nontronite, from Krivan, near Moraviczka, in the Banat.

B. H. B.

**Eudnophite.** By DES-CLOIZEAUX (*Jahrb. f. Min.*, 1885, **1**, Ref., 195).—The author describes the form and optical characters of an oblong prismatic fragment of eudnophite from Kangerdluarsuk in Greenland, more transparent than the eudnophite of Brevig in

Norway. As horizontal or crossed dispersion could never be observed, the mineral is probably rhombic and not monoclinic. B. H. B.

**Triclinic Felspar from Quatre Ribeiras.** By FOUQUÉ (*Jahrb. f. Min.*, 1885, 1, Ref., 191—193).—Although the crystals from Quatre Ribeiras, in the Island of Terceira, are but 2 mm. long and broad, and 1 mm. thick, the author has submitted them to a complete crystallographic and optical examination. The crystals occur in a dark volcanic rock; they are colourless and free from inclusions. The density is 2·5937. In Thoulet's solution of sp. gr. 2·5927 at 18° the entire mass sinks, at 14·2° about one half sinks; the latter has the composition given under I, the portion which did not fall to the bottom had the composition II:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.
I.	68·73	19·76	1·12	9·45	1·37	100·43
II.	67·86	19·79	1·60	8·67	2·26	100·18

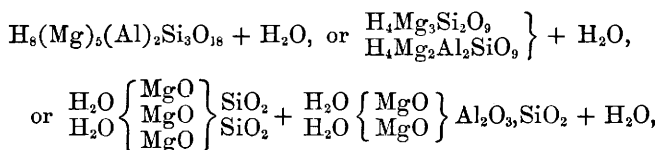
The felspar is thus chemically analogous to orthoclase and albite. This remarkable felspar is triclinic, and crystallographically resembles most microcline. It is not only different from orthoclase and from all the known plagioclases, but also takes no place in Tschermak's felspar series. Crystallographically and optically it approaches several of the felspars of Pantelleria (*Abstr.*, 1884, 1104), but differs from them chemically by the absence of the anorthite-compound and the corresponding high percentage of silica. B. H. B.

**The Percentage of Water in Clinocllore.** By P. JANNASCH (*Jahrb. f. Min.*, 1885, 1, Mem., 92—95).—In order to ascertain the nature of the combination in which water occurs in clinocllore, the author selected for examination the clinocllore from the Mussa Alp; the analysis of which gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	H <sub>2</sub> O.	Na <sub>2</sub> O.
29·31	21·31	0·07	3·24	31·28	14·58	0·43
	Li <sub>2</sub> O.		Total.		Density.	
	trace		100·22		2·555	

From a number of determinations of the loss on ignition, of the loss of water at various temperatures, and direct weighings of the water, the author concludes that clinocllore contains a total of 5 mols. H<sub>2</sub>O, and not 4 as formerly believed; further that a portion of the water present (about 1 mol.) is loosely combined, and is partly given up over concentrated sulphuric acid; and, lastly, that 4 mols. H<sub>2</sub>O are only driven off on ignition. Of this latter amount, about 1 mol. is very firmly retained, being driven off only at a high temperature. One equivalent must, therefore, be regarded as water of crystallisation, and 4 mols. as water of constitution. Clinocllore, then, has the following composition:—





in which a portion of  $\text{Al}_2\text{O}_3$  is replaced by  $\text{Fe}_2\text{O}_3$ , and a portion of  $\text{MgO}$  by  $\text{FeO}$ .  
B. H. B.

**New Mineral from the Environs of Nantes.** By A. DAMOUR (*Jahrb. f. Min.*, 1885, **1**, Ref., 194—195).—The occurrence of a new mineral at Barbin has already been mentioned (Abstr., 1884, 408). The mineral is rhombic. It occurs planted on quartz or felspar in pegmatite veins in gneiss, isolated or in druses with apatite, arsenical pyrites, and iron pyrites. The crystals are yellowish;  $H. = 6$ ; density 2.586. On ignition it loses 6 to 7 per cent. of water. The analysis gave the following results:—

$\text{SiO}_2$ .	$\text{BeO}$ .	$\text{H}_2\text{O}$ .	$\text{FeO}$ .	Total.
49.26	42.00	6.90	1.40	99.56

The author suggests for the mineral the name of *Bertrandite*, after its discoverer.  
B. H. B.

**Boric Acid in Mica.** By F. SANDBERGER (*Jahrb. f. Min.*, **1**, Mem., 171).—Analyses of micas, in connection with the author's researches on ore-veins, have recently given a remarkable result. In a number of micas, he found a small percentage of boric acid. Distinct reactions were obtained with the following: dark potassium iron mica from the gneiss of Schapbach and Wolfach in the Black Forest, dark potassium iron mica from the granite of Wittichen in the Black Forest, and Niederpfannenstiel in the Erzgebirge, dark lithium mica from the lithonite granite of Röslau, lithionite from the pegmatite of Tröstau, phlogopite from the granular limestone of Scheelingen and Ontario in Canada, potassium mica from the granite of Aschaffenburg, rubellan from the basalt tuff of Aschaffenburg and Pöllma. The most distinct reaction was given by the rubellan and lithionite of Tröstau. The author concludes that boric acid will be found to be present in all micas.  
B. H. B.

**Chrysocolla from Etna.** By G. FREDÀ (*Gazzetta*, **14**, 339—340). As Waltershausen has described atacamite as occurring in green globular concretions on the lava of Monti Rossi, near Nicolosi, the author here states that a few years ago he found similar concretions to consist of chrysocolla. On repetition of his former analyses the following results were obtained:—

$\text{CuO}$ .	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3, \text{FeO}_3, \text{CaO}$ .	$\text{H}_2\text{O}$ .
44.43	35.41	traces	18.72

These point to a composition not widely different from that of chrysocolla,  $\text{CuO}, \text{SiO}_2, 2\text{H}_2\text{O}$ .  
V. H. V.

**Labradorite Rock of the Coasts of Labrador.** By E. COHEN (*Jahrb. f. Min.*, 1885, 1, Mem., 183—185).—The description of the Labrador rocks, recently published by Wichmann, has induced the author to publish some older observations. Some years ago he found at Walldkirch fragments of rock, sent from Labrador, cast aside as useless. The rock appeared to be an aggregate of plagioclase (labradorite), and diallage with biotite, iron pyrites, magnetite, and ilmenite. Under the microscope, hypersthene, quartz, and hornblende, were also observed to be present. Assuming that the rock is eruptive, it must be classed as a gabbro with biotite, hypersthene, and quartz, as accessory constituents. The mineralogical constitution of the labradorite rock is very variable, and the large pieces of pure labradorite which are used as ornamental stones, indicate a very irregular texture. As these peculiarities are much more characteristic of the crystalline schists than of the true massive rocks, the author concludes that it is not so certain that the rock belongs to the latter class, as Wichmann is inclined to assume. B. H. B.

**Origin of Iron, Manganese, and Zinc Minerals in the Older Limestones of the Secondary Series.** By DIEULAFAIT (*Compt. rend.*, 100, 662—664).—In 338 specimens of the calcareous rocks at the base of the secondary series round the central plateau of the Cevennes, zinc and manganese could be easily detected in 10 grams of the rock. The author has previously shown that metalliferous minerals are disseminated throughout the primary rocks on which the secondary rocks rest. The waters of the inland seas in which the secondary rocks were deposited would contain sensible quantities of zinc, manganese, and other metals, dissolved from the older rocks. As soon as any limestone was formed, it would react with the iron in solution, precipitating it in the form of oxide, and hence the latter is always found more abundantly in the earlier beds. The zinc and manganese would remain in solution, and would impregnate and become disseminated throughout the limestones subsequently formed.

C. H. B.

**Deposit from a Spring at Carmaux.** By S. MEUNIER (*Compt. rend.*, 100, 665—667).—In a gallery of a mine at Carmaux a stream of water with a temperature of 18° flows through a fissure which is lined with somewhat large colourless crystals of calcite and which contains a gelatinous substance of peculiar appearance. The water contains 0.34 gram per litre of solid matter, with the following percentage composition:  $\text{CaCO}_3$  57.6,  $\text{SiO}_2$  18.1,  $\text{NaCl}$  24.3. The gelatinous matter, when dried at 100°, has the sp. gr. 1.75, and is entirely amorphous. It melts easily before the blowpipe to a vesicular glass, and when treated with hydrochloric acid, it effervesces violently with separation of flakes which resemble gelatinous silica, but which, when dried, are as fusible as the original substance. The effervescence is due to the presence of small crystals of calcite irregularly disseminated throughout the gelatinous substance. The gelatinous mineral can be decomposed by fusion with barium carbonate, and has the composition  $\text{SiO}_2$  42.30,  $\text{CaO}$  30.28,  $\text{Fe}_2\text{O}_3$  4.12,  $\text{Na}_2\text{O}$  0.09,  $\text{H}_2\text{O}$  22.50 = 99.29, thus resembling plombierite, from

which, however, it differs in many of its properties. When dried, the mineral shrinks considerably, becoming opaque and greyish, or milk-white, with a fibrous structure resembling that of papier maché or some forms of asbestos. If the dried substance is placed in water it resumes precisely its original appearance. This drying and regelatinisation can be repeated many times. The mineral is not sensibly attacked by boiling hydrochloric acid.

C. H. B.

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## Organic Chemistry.

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**Action of Chlorine on Butylenes.** By CHÉCHOUKOFF (*Bull. Soc. Chim.*, **43**, 127—128, comp. Abstr., 1884).—On heating isopropenyl carbinol with a small quantity of acid, isobutaldehyde is formed. Hydrogen iodide at 0° converts the carbinol into tertiary butyl iodide. By the action of alcoholic potash at 140—150° on isobutyl chloride, ethylic ether is produced and not isobutylene. By the action of hydrogen chloride on isobutyl chloride, isobutylene chloride,  $C_4H_8Cl_2$ , boiling at 106—107° is obtained; this, by the action of potassium carbonate, is converted into isobutylene glycol, boiling at 177° to 178°. By acting on pure pseudobutylene with chlorine, the additive compound pseudobutylene chloride, boiling at 112° to 114°, alone has been obtained. The author confirms the fact observed by Konovaloff, that the butylene prepared by Perchoff's method is a mixture of the pseudo- and iso-butylenes. A. P.

**Condensation of Crotonylenes.** By FAVORSKY (*Bull. Soc. Chim.*, **43**, 112).—If the product of the reaction between phosphorous pentachloride and ethyl methyl ketone is treated with potash, either of the crotonylenes,  $C_2Me_2$  or  $C_2HEt$ , may be obtained at will by slightly modifying the conditions. A. P.

**Action of Chlorine on Tetramethylethylene.** By LOUPOTSKY (*Bull. Soc. Chim.*, **43**, 13).—By the action of chlorine on tetramethylethylene, the compound  $C_6H_{11}Cl$ , boiling at 113—115°, is obtained; this, on treatment with an excess of water at the ordinary temperature, is converted into a non-saturated alcohol, which resembles Pavloff's dimethyl isopropyl carbinol, both in its odour and boiling point. It combines with bromine, without the formation of hydrogen bromide, to form a compound of the composition  $C_6H_{11}Br_2OH$ ; with acetic acid, it yields a non-saturated compound, and by the action of weak acids it is transferred into pinacolone. It probably has the composition  $HO \cdot CMe_2 \cdot CMe : CH_2$ . A. P.

**Action of Sulphuric Acid on Cyanogen Iodide.** By E. GOSSIN (*Bull. Soc. Chim.*, **43**, 98).—If a dish containing cyanogen iodide is placed above a vessel of concentrated sulphuric acid covered with a

bell-jar, in the course of a few days the whole of the cyanogen iodide will be decomposed, and crystals of iodine found at the bottom of the sulphuric acid. A. P.

**Cyanmethethine.** By C. RIESS and E. v. MEYER (*J. pr. Chem.* [2], **31**, 112—116).—*Cyanmethethine*,  $C_8H_{13}N_3$ , is obtained, together with cyanethine, by the action of sodium on a mixture of 2 mol. ethyl cyanide and 1 mol. methyl cyanide. After the action of the sodium is completed, the excess of cyanide is distilled off, the solid residue next digested with water, and the insoluble residue submitted to fractional crystallisation from alcohol. The fourth fraction consists of almost pure cyanmethethine, which crystallises from benzene in shining, rhombic leaflets, melting at  $165.5^\circ$ , and subliming at temperatures below  $100^\circ$ . It is easily soluble in alcohol, and sparingly soluble in benzene and ether; 1 part dissolves in 35 parts of water at  $20^\circ$ , forming an alkaline solution. It is volatile in steam. It forms an *aurochloride*,  $C_8H_{13}N_3 \cdot HAuCl_4$ , crystallising in yellow rectangular leaflets, and a *platinochloride*,  $(C_8H_{13}N_3)_2 \cdot H_2PtCl_6$ , crystallising in aggregates of needles. With silver nitrate, it forms a compound having the composition  $(C_8H_{13}N_3)_2 \cdot AgNO_3$ , which is soluble in hot dilute alcohol, from which it separates in small crystals. With bromine, it forms *monobromocyanmethethine*,  $C_8H_{12}BrN_3$ ; this is soluble in water, alcohol, ether, and benzene, from which it crystallises in rhombic crystals, melting, with decomposition, at  $155^\circ$ . On warming, this compound gives an odour resembling that of the corresponding bromocyanethine.

Cyanmethethine heated for some hours with concentrated hydrochloric acid at  $180^\circ$  gives off ammonia, and is converted into a compound melting at  $150^\circ$ ; this appears to be a *hydroxy-base* of the formula  $C_8H_{11}N_2 \cdot OH$ . P. P. B.

**Pyrotartaronitrile and Succinonitrile.** By L. HENRY (*Compt. rend.*, **100**, 742—745).—The *pyrotartaronitrile*,  $CN \cdot CH \cdot CH_2 \cdot CH_2 \cdot CN$ , has hitherto not been isolated, but only used in the crude state for conversion into the carboxylic acid. It may readily be prepared by the action of pure potassium cyanide on trimethylene bromide; thus obtained, it is a colourless viscid liquid, boiling at  $274^\circ$ , of sp. gr. 0.9961 at  $11^\circ$ , soluble in water, alcohol, and chloroform, insoluble in ether.

*Succinonitrile*,  $CN \cdot CH_2 \cdot CH_2 \cdot CN$ , is most readily obtained by means of pure potassium cyanide containing hydrocyanic acid. The author's observations regarding its physical and chemical properties are in accordance with those of Norton and Tchermiak; he considers however that it is not amorphous, but a confusedly crystalline substance.

V. H. V.

**Characteristic Reaction of Secondary Alcohols.** By G. CHANCEL (*Compt. rend.*, **100**, 601—603, comp. Abstr., 1883, 914).—Secondary hexyl alcohol prepared from mannitol by Erlenmeyer and Wanklyn's method (*Annalen*, **165**, 146), yields butyl-nitrous acid when treated with nitric acid; and secondary octylic alcohol, obtained by the action of potash on castor-oil, yields hexyl-nitrous acids.

*Hexyl-nitrous acid*, obtained in the free state by the action of hydro-

chloric acid on the potassium salt, is a colourless oily liquid, which boils with partial decomposition at  $212^{\circ}$ , under a pressure of 763 mm. The author has determined the sp. gr. at every  $5^{\circ}$  between  $0^{\circ}$  and  $40^{\circ}$ ; sp. gr. at  $0^{\circ}$  compared with water at  $4^{\circ} = 1.1381$ . When treated with reducing agents, it is converted into normal caproic acid. Potassium and silver hexyl-nitrites are crystalline salts, only slightly soluble in water; they decompose without detonation when heated, and in this respect differ from their lower homologues. The silver salt when carefully heated, leaves a residue of filiform metallic silver.

Butyl-nitrous acid from secondary hexyl alcohol yields normal butyric acid when treated with reducing agents. The formation of alkyl-nitrous acids takes place with all secondary alcohols excepting isopropyl alcohol. A small quantity of the alcohol under examination is treated with about 1 c.c. of nitric acid, mixed with water and agitated with ether. The ethereal solution is collected on a watch-glass, the ether allowed to evaporate, and the residue dissolved in alcohol and mixed with a few drops of alcoholic potash. If the alcohol is a secondary alcohol, a potassium alkyl nitrite will separate in small yellow prisms.

C. H. B.

**Action of Hydrochloric Acid on Isopropenyl Carbinol.** By LWOFF and CHECHOUKOFF (*Bull. Soc. Chim.*, **43**, 112 — 113).—By the action of dilute hydrochloric acid on isopropenyl carbinol,  $\text{CH}_2:\text{CMe}\cdot\text{CH}_2\cdot\text{OH}$ , at the ordinary temperature, isobutylene glycol,  $\text{HO}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ , is formed, together with the aldehyde  $\text{CHMe}_2\cdot\text{CHO}$ . By the action of water at high temperatures, the glycol is transformed into the aldehyde.

A. P.

**Glycide of Hexylic Glycerol.** By KABLOUKOFF (*Bull. Soc. Chim.*, **43**, 111).—The compound obtained by treating the acetate of *butyl allyl methyl carbinol* first with hypochlorous acid and afterwards with a concentrated aqueous solution of potash, is probably the glycide of hexylic glycerol,  $\text{CH}_2\cdot\overset{\text{O}}{\text{CH}}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ . It is a very mobile liquid, boiling at  $176$ — $178^{\circ}$ ; it is soluble in water, reduces an ammoniacal solution of silver oxide, and does not form a crystalline compound with hydrogen sodium sulphite.

A. P.

**Milk-sugar and Galactose.** By W. H. KENT and B. TOLLENS (*Annalen*, **227**, 221—232).—Some of the results contained in this paper have already appeared (Abstr., 1884, 980). Levulinic acid is formed together with formic acid, on heating galactose with hydrochloric acid. The authors consider it probable that all true carbohydrates yield levulinic acid when heated with mineral acids. Mucic acid does not show a constant melting point. When heated with water at  $175$ — $180^{\circ}$ , mucic acid yields paramucic acid, pyromucic acid, dehydromucic acid, and other substances.

A. J. G.

**Action of Amines on Methaldehyde.** By KOLOTOFF (*Bull. Soc. Chim.*, **43**, 112).—Methaldehyde does not act on triethylamine; but on agitation with diethylamine it gives a liquid of the formula

$\text{CH}_2(\text{NEt}_2)_2$ , boiling at  $166\text{--}169^\circ$ . Ethylamine, under the same circumstances, yields a liquid,  $\text{CH}_2:\text{NEt}$ , boiling at  $205\text{--}208^\circ$ , and aniline gives a crystalline substance,  $\text{CH}_2:\text{NPh}$ , melting at  $138^\circ$ . All the above compounds, when treated with water, are reconverted into methaldehyde and the corresponding amine. A. P.

**Glyoxal-ammonium Hydrogen Sulphite.** By DE FORCRAND (*Compt. rend.*, **100**, 642—644).—The author has prepared and carefully purified a considerable quantity of glyoxal-ammonium hydrogen sulphite. It forms colourless brilliant flattened prisms, which have the composition  $\text{C}_2\text{H}_2\text{O}_2(\text{NH}_4)_2\text{O}, 2\text{SO}_2, \text{H}_2\text{O}$ , and are thus strictly analogous to the other glyoxal bisulphites. Towards the end of the evaporation of the mother-liquor from these crystals, a small quantity of a confusedly crystalline substance is deposited. This contains 21.57 per cent. of  $(\text{NH}_4)_2\text{O}$ , and is possibly the anhydrous glyoxal-ammonium sulphite described by Debus and referred to by Engel (*Abstr.*, 1884, 729). C. H. B.

**Iodoacetone.** By P. DE CLERMONT and P. CHAUTARD (*Compt. rend.*, **100**, 745—747).—When treated with iodine in the presence of iodic acid, acetone is converted into a moniodo-derivative,  $\text{CMeO}\cdot\text{CH}_2\text{I}$ ; but in order to obtain a satisfactory yield, certain precautions are necessary, which are given in detail in the original memoir. This substance is a volatile corrosive liquid, of sp. gr. 2.17 at  $15^\circ$ , decomposing slowly in the presence of sunlight, but more rapidly when heated. An impurity of acetone in this substance may be readily detected by means of the iodoform reaction. Mineral acids convert it readily into symmetrical diiodoacetone,  $\text{CH}_2\text{I}\cdot\text{CO}\cdot\text{CH}_2\text{I}$ ; with potassium acetate it yields an ethereal salt of acetic acid,  $\text{CMeO}\cdot\text{CH}_2\cdot\text{OAc}$ , whilst silver chloride converts it into monochloroacetone. V. H. V.

**Acetonechloroform, Acetonebromoform, and the Action of Solid Potash on a Solution of Iodoform in Acetone.** By C. WILLGERODT and A. MÜLLER (*Chem. Centr.*, 1884, 808).—Acetonebromoform is best prepared by dissolving 5 grams of bromoform in 30 grams of acetone, and gently digesting this mixture with 5—10 grams of powdered soda-lime. The acetonebromoform may be separated from unchanged bromoform, by fractioning in a current of steam, the bromoform coming over first. Acetonebromoform closely resembles acetonechloroform, and when free from water melts at  $175^\circ$ , and may be sublimed. It exists also in a hydrated form, which melts at  $165\text{--}167^\circ$ . It is insoluble in water, readily soluble in organic solvents. Willgerodt is now experimenting on the physiological behaviour of acetonechloroform. This substance produces anæsthesia in small, and death in large doses. Willgerodt has not yet succeeded in obtaining acetoneiodoform. When solid potash acts on iodoform dissolved in acetone, the principal product is methylene iodide.

L. T. T.

**Double Uranium Acetates.** By C. RAMMELSBERG (*Ann. Phys. Chem.* [2], **24**, 293—318).—Uranyl acetate forms with other metallic acetates a series of well-defined double salts, many of which have

been described by Duflos, Wertheim, and Weselsky. In this paper the crystallographic form and its relations to composition of these salts are minutely examined. These salts may be divided into a few characteristic groups, the salts of which are isomorphous.

I. *Alkaline uranyl acetates* of the general formula  $M'O\overline{Ac}, UO_2(O\overline{Ac})_2$ , which, with the exception of the thallium salt, contain one atom of the metal to one of uranium; the sodium and the ammonium salts are anhydrous; the potassium and silver salts contain 1 mol.  $H_2O$ . The sodium salt belongs to the regular, the rest to the quadratic system; the potassium and silver salts are isomorphous; an octohedron of the silver salt with axial ratio  $a : a : \frac{5}{6}c$  corresponding to that of the potassium salt with axial ratio  $a : a : c$ .

II. *Acetates of uranyl and the alkaline earths* of general formula  $M''(O\overline{Ac})_2, 2UO_2(O\overline{Ac})_2 + 6H_2O$ , form an isomorphous group.

III. *Acetates of uranyl and other dyad metals* are separable into three sub-groups of general formula,  $M''(O\overline{Ac})_2, UO_2(O\overline{Ac})_2 + 6H_2O$ ;  $M(O\overline{Ac})_2, 2UO_2(O\overline{Ac})_2 + 7H_2O$ ; and  $M(O\overline{Ac})_2, 2UO_2(O\overline{Ac})_2 + 12H_2O$ , all of which crystallise in the trimetric system. To the first class belong a manganese and a cadmium salt, with an axial ratio  $0.63 : 1 : 0.39$ ; to the second class belong magnesium, zinc, nickel, cobalt, and iron salts, with an axial ratio of  $0.875 : 1 : 0.95$ ; and to the third class belong a magnesium and a manganese salt with an axial ratio  $0.75 : 1 : 0.5$ .

As regards the method used for the analyses of these salts, some remarks are added with reference to the separation of the other metals from uranium. The alkali metals are best separated by heating the alkali uranate,  $M_2U_2O_7$ , with ammonium chloride in a current of hydrogen. From the resultant substance, water extracts the chloride of the alkali; thallium is precipitated by potassium iodide; the alkaline earths and lead by sulphuric acid in presence of alcohol. It is separated from magnesium by ammonium sulphide, from manganese and zinc by decomposition of the solution with excess of ammonium carbonate, and subsequent precipitation with ammonium sulphide. Nickel and cobalt can be separated by barium carbonate, but this method cannot be applied in the case of magnesium and zinc. Cadmium and copper can be separated by hydrogen sulphide and can be determined as sulphides.

V. H. V.

**Perkin's Reaction in the Paraffin Series.** By A. SCHNEEGANS (*Annalen*, **227**, 79—96).—*Nonylenic acid*,  $C_6H_{13}\cdot CH : CH \cdot COOH$ , is obtained in small quantity by heating a mixture of cœnanthaldehyde with acetic anhydride and sodium acetate at  $160$ — $170^\circ$  for 30 hours. It forms a colourless oily liquid of tallow-like odour, scarcely soluble in water. It distils readily with steam, but cannot be distilled alone at the ordinary pressure without some decomposition. The calcium, barium, silver, and lead salts are described. Nascent hydrogen has no action on the acid, which, however, unites with hydrobromic acid to form bromononylic acid,  $C_6H_{13}Br \cdot COOH$ , a thick pale yellow liquid, soluble in soda to a clear solution; this, on gently heating, is decomposed with separation of an oil, probably an octylene.

An *octylenic acid*,  $C_8H_{14}O_2$ , was prepared in manner similar from valeraldehyde, but was not further examined.



Hexylparaconic acid,  $\text{CO} \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \\ | \\ \text{O} - \text{CH} \cdot \text{C}_6\text{H}_{13} \end{array}$ , is obtained by heating a

mixture of cenanthaldehyde, acetic anhydride, and sodium succinate for 20 hours at 110–120°. It crystallises in long thin colourless needles, melts at 89°, and is sparingly soluble in cold water, moderately soluble in alcohol, ether, chloroform, and carbon bisulphide. It is monobasic; the calcium and silver salts are described. When heated with bases, salts of the dibasic *hexitamalic acid* are obtained; of these, the calcium salt,  $\text{C}_{11}\text{H}_{18}\text{O}_5\text{Ca}$ , the barium salt,  $\text{C}_{11}\text{H}_{18}\text{O}_5\text{Ba}$ , and the silver salt,  $\text{C}_{11}\text{H}_{18}\text{O}_5\text{Ag}$ , are described. When distilled, hexylparaconic acid is decomposed into carbonic anhydride, decylenic acid, and, in small quantity, hexylbutyrolactone.

*Decylenic acid*,  $\text{C}_9\text{H}_{17}\cdot\text{COOH}$ , forms a colourless oil at ordinary temperatures, but can be solidified on cooling, and then melts at 10°; it is readily volatile with steam. It is not identical with the other acids of the same empirical formula that have been previously described. The barium salt,  $(\text{C}_{10}\text{H}_{17}\text{O}_2)_2\text{Ba}$ , crystallises in colourless needles; the calcium and silver salts were also prepared. When treated with hydrobromic acid, the free acid is converted into *bromocapric acid*, a pale yellow oil heavier than water.

*Hexylbutyrolactone* (decylactone),  $\text{C}_{10}\text{H}_{18}\text{O}_2$ , is most readily prepared by the action of dilute aqueous sodium carbonate on bromocapric acid. It is a colourless oil, of peculiar soap-like odour, and is very sparingly soluble in water.

$\gamma$ -*Hydroxydecylic acid*,  $\text{C}_6\text{H}_{13}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , is obtained by heating decylactone with baryta-water; it is crystalline, and is very readily reconverted into decylactone and water. The barium salt,  $(\text{C}_{10}\text{H}_{19}\text{O}_3)_2\text{Ba} + \text{H}_2\text{O}$ , crystallises in stellate groups of rhombic tables. The silver salt,  $\text{C}_{10}\text{H}_{19}\text{O}_3\text{Ag}$ , forms small white needles.

A. J. G.

**Homologues of Glycidic Acid.** By MELIKOFF (*Bull. Soc. Chim.*, 43, 115).—Propyleneoxycarboxylic acid crystallises in rhombic prisms, and melts at 84°. It is soluble in ether and in water, and is unaltered by the air; it does not give a red colour with ferric salts. The chlorhydroxybutyric acid obtained from this compound (*Abstr.*, 1884, 1301) crystallises in long prisms, melts at 62–63°, is unaltered by exposure to air, is not hygroscopic, and dissolves in all proportions in water, alcohol, and ether; the zinc and calcium salts have been obtained. By the action of alcoholic potash, propyleneoxycarboxylic acid is obtained. Propyleneoxycarboxylic acid is acted on by hydrogen bromide, bromhydroxybutyric acid being formed. This compound crystallises in long prisms, melts at 90°, and is identical with the acid obtained by Kolbe by the action of water on dibromobutyric acid. The chlorhydroxyisobutyric acid obtained by the action of hydrogen chloride on metoxyacrylic acid is identical with the acid obtained by the action of hypochlorous acid on *metacrylic acid*. Bromhydroxyisobutyric acid obtained in a similar manner crystallises in long prisms, melts at 101°; is insoluble in water, alcohol, and ether, and is identical with Kolbe's iso-acid. By treating metoxyacrylic acid with ammonia, the ammonium salt of *amidohydroxyisobutyric acid* is

obtained. The free acid formed on treating the lead salt with hydrogen sulphide crystallises in microscopic crystals, is only slightly soluble in water, and is isomeric with amidohydroxybutyric acid; it forms compounds with acids. The chloride,  $C_4H_9NO_3HCl$ , forms large prisms, soluble in water.

On heating metoxyacrylic acid with water at  $100^\circ$ ,  $\alpha$ -methylglyceric acid is obtained, crystallising in prisms; it melts at  $100^\circ$ , is easily soluble in water, and slightly so in ether; the potassium, calcium, and silver salts have been prepared. When the potassium salts of glycidic, metoxyacrylic, or propyleneoxycarboxylic acids are heated in sealed tubes, with equal quantities of water, the two first acids are soon entirely transformed into the potassium salts of the corresponding glyceric acids, whilst it is necessary to heat it for 16 hours to effect a similar transformation in the case of the propyleneoxycarboxylic acid. By the action of hypochlorous acid on isocrotonic acid, an uncrystallisable liquid is obtained; on saturating this with zinc carbonate, two zinc salts are formed: one is crystalline, and yields a chlorhydroxybutyric acid identical with the compound obtained by the action of hydrogen chloride on propyleneoxycarboxylic acid, whilst the second zinc salt forms a resinous mass, and yields a liquid acid, which is difficultly crystallisable, and by the action of alcoholic potash is converted into the potassium salt of butylglycidic acid; the free acid is a thick liquid; it combines with the elements of water, forming an acid similar to that described by Hanriot as butylglyceric acid; when acted on by hydrogen chloride, this acid yields chlorhydroxyisobutyric acid.

A. P.

**Ethylic  $\gamma$ -Hydroxyvalerate and  $\gamma$ -Hydroxyvaleramide.** By E. L. NEUGEBAUER (*Annalen*, **227**, 97—106).—*Ethylic  $\gamma$ -hydroxyvalerate*,  $HO \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot COOEt$ , is prepared by dissolving valerolactone in a slight excess of soda, neutralising with nitric acid, adding silver nitrate, and digesting the silver normal  $\gamma$ -hydroxyvalerate so formed with about three-fourths of the calculated amount of ethyl iodide. It forms a colourless mobile liquid of faint ethereal odour, is soluble in alcohol and ether, but insoluble in water. On distillation it is in great part decomposed into alcohol and valerolactone.

*$\gamma$ -Hydroxyvaleramide*,  $HO \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CONH_2$ , is obtained by the action of gaseous ammonia, or better, of alcoholic ammonia, on ethylic  $\gamma$ -hydroxyvalerate; it is also readily formed by the action of alcoholic ammonia on valerolactone. It crystallises in white plates, melts at  $50^\circ$ , is soluble in water and alcohol, and insoluble in ether, benzene, and carbon bisulphide. Ammonia is evolved when it is heated at  $110^\circ$ , and at  $206^\circ$  valerolactone distils, accompanied by very small quantities of the amide. It is decomposed by acids and bases.

A. J. G.

**Action of Phosphorus Pentachloride on Succinyl Compounds and on Tartaric Acid.** By E. KAUDER (*J. pr. Chem.* [2], **31**, 1—36).—By the action of phosphorus pentachloride in excess on succinic acid at  $230^\circ$ , a liquid is obtained having the composition  $C_4Cl_6O$ , and boiling at  $194$ — $214^\circ$ ; it is a mixture of two isomerides, for by distillation with steam a solid substance is isolated, melting at

41°, boiling at 209°, and also having the composition  $C_4Cl_6O$ . Either the liquid or the solid modification, when heated with strong sulphuric acid, yields a white very hygroscopic crystalline substance; this when heated loses water, and yields a sublimate of an anhydride,  $C_4Cl_2O_3$ , melting at 119·5°, and easily reconverted into the original hygroscopic acid; these two substances seem to be *dichloromaleic acid*,  $C_2Cl_2(COOH)_2$ , and *dichloromaleic anhydride*,  $C_2Cl_2(CO)_2O$ . The silver and dimethyl salts of the acid are described (compare Ciamician, *Ber.*, **16**, 2396). Neither of the chlorides  $C_4Cl_6O$  are decomposed by contact with water, or even by aqueous soda; no clue to their constitutions was obtained by the action of reducing agents. The action of ammonia on the liquid chloride is very energetic; a liquid boiling at 210—240°, free from nitrogen, is first formed; by further action of ammonia at 140° the whole is decomposed. The solid chloride scarcely reacts with ammonia, until heated above 130°. Ethylamine decomposes the liquid, but not the solid chloride. Aniline in alcoholic solution reacts with the liquid chloride, yielding an anilidic acid; the solid chloride is not acted on. The liquid and solid chlorides may be called  $\alpha$ - and  $\beta$ -*dichloromaleic tetrachloride* respectively, but the function of the oxygen-atom cannot be determined. This last atom of oxygen may be removed by the further action of phosphorus pentachloride, but the molecule is then resolved into 2 mols. of hexachlorethane.

Phosphorus pentachloride acts on phenyl-succinimide, forming *dichloromaleic phenylimide*,  $ClCl_2:(CO)_2:NPh$ , melting at 201°, and subliming easily, and a perfectly amorphous body of unknown composition.

Chlorine acts readily on succinyl chloride; the product, after heating with excess of methyl alcohol, deposits needles of methyl fumarate,  $C_2H_2(COOMe)_2$ . This method may be used for the preparation of fumaric acid. By precipitating the mother-liquor with water, *methyl monochlorofumarate*,  $C_2HCl(COOMe)_2$ , is obtained as an oil, boiling at 223—225°. By the action of water on the crude product obtained from succinic chloride, a mixture of fumaric, monochlorofumaric, and dichloromaleic acids is formed, from which *monochlorofumaric acid*,  $C_2HCl(COOH)_2$ , may be isolated by repeated recrystallisation. It melts at 191°, without the formation of an anhydride, and is very soluble in water.

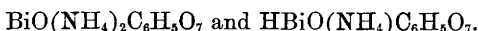
By acting with phosphorus pentachloride on tartaric acid, and with methyl alcohol on the product, which contains *monochlorofumaryl chloride*,  $C_2HCl(COCl)_2$ , methyl monochlorofumarate is obtained. The ethyl salt has been similarly prepared by Perkin and Duppa, but described as being derived from maleic acid. Monochloromaleic acid has, however, been prepared by Carius; it melts at 171—172°, and easily forms an anhydride; further, it is distinguished from monochlorofumaric acid by the different solubilities and amounts of water of crystallisation contained in its salts. Carius describes the salts,  $COOK \cdot C_2HCl \cdot COOH + H_2O$  and  $C_2HCl(COO)_2Ba + 5H_2O$ , whereas monochlorofumaric acid yields the salts  $COOK \cdot C_2HCl \cdot COOH$  and  $C_2HCl(COO)_2Ba + 3H_2O$ ; the silver salt is also described.

H. B.

**Vinaconic Acid.** By F. RÖDER (*Annalen*, **227**, 13—25).—The results of this investigation have been to some extent published by the author and Fittig (*Abstr.*, 1883, 730; 1884, 295). The name vinylmalonic acid, formerly proposed for the acid, is now replaced by *vinaconic acid*. The preparation of vinaconic acid from ethylene bromide and ethylic sodomalonate has been already described. It crystallises in thin needles melting at 139°. The *barium* salts,  $C_5H_4O_4Ba$  and  $(C_5H_5O_4)_2Ba + 4H_2O$ , and *silver* salts,  $C_5H_4O_4Ag_2$  and  $C_5H_5O_4Ag$ , are described. Bromethylmalonic acid (*loc. cit.*) forms nodular crystals melting at 116°. Vinaconic acid when distilled yields butyrolactone and carbonic anhydride. A. J. G.

**Constitution of Vinaconic Acid.** By R. FITTIG (*Annalen*, **227**, 25—31).—The author points out that Perkin's trimethylenedicarboxylic acid (*Abstr.*, 1884, 832) is identical with Röder's vinaconic acid (preceding Abstract). He disputes the accuracy of the formula  $\begin{smallmatrix} CH_2 \\ < \\ CH_2 \end{smallmatrix} C(COOH)_2$ , assigned to the acid by Perkin, and regards the evidence as pointing to the constitution  $CH_2 : CH \cdot CH(COOH)_2$ . A. J. G.

**New Compounds of Bismuth.** By A. CAVAZZI (*Gazzetta*, **14**, 289—291).—*Neutral bismuth citrate*,  $BiC_6H_5O_7$ , is obtained as a white granular powder by boiling together solutions of bismuth nitrate and citric acid; it dissolves readily in ammonia, and from the solution there separates a basic bismuth citrate in the form of a gelatinous precipitate. On boiling the neutral bismuth citrate with ammonia, according to the conditions of the reaction, there are obtained two ammonium bismuth citrates,



*Basic bismuth phosphate*,  $2BiPO_4, 3Bi_2O_3$ , is obtained by precipitating an ammoniacal solution of bismuth citrate by sodium phosphate; it is a white powder, insoluble in water, soluble in hydrochloric and nitric acids; it is infusible, but readily reduced.

*Basic bismuth arsenate*,  $2BiAsO_4, 3Bi_2O_3$ , obtained in manner similar to the phosphate, is a gelatinous substance, resembling the phosphate in its properties. V. H. V.

**Levonic Acid.** By B. WIEDERHOLD (*Chem. Centr.*, 1884, 971—972).—The author gives this name to an acid which he has obtained by heating levulose with baryta-water or solid barium hydroxide. The acid is a yellowish-brown powder, of the composition  $C_{14}H_{12}O_8 + 3H_2O$ , which is decomposed on heating. It is easily soluble in alcohol and water. Many of its salts were examined, but they are mostly basic, and not very well characterised. L. T. T.

**Atropaic Acid, a new Organic Acid from the Sugar-cane.** By W. SAVARY (*Chem. Centr.*, 1884, 968—969).—The author has isolated this acid from the lime-sludge obtained in the manufacture of sugar. The lime was accurately determined, and just enough sulphuric acid and water stirred in to yield crystalline gypsum. The

dry porous mass was then extracted with boiling alcohol, when the above, and other organic acids were dissolved out. The acid in question was isolated by means of its ethyl salt, which boils at about 184—188°. When pure, *atripaic acid* forms monoclinic prisms of the formula  $C_6H_6O_{12} + 6H_2O$ , which lose water at 100° and leave *atripaic acid hydrate* as a white powder. The acid melts at 98° in its water of crystallisation, and when heated more strongly, partly sublimes in the form of its anhydride, but the greater portion is decomposed. It forms crystalline salts with the alkalis, insoluble salts with the alkaline earths. The author considers the formula of the anhydride to be  $C_6(HO)_6O_6$ . When treated with sodium amalgam it did not, however, yield grape-sugar, as the author expected, but hydroxycitric acid,  $C_6H_8O_8$ . The author is continuing his researches on this acid.

L. T. T.

**Decomposing Action of Aluminium Chloride on Hydrocarbons.** By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, 100, 692—698).—On heating hydrocarbons which contain both aromatic and paraffinoid groups with aluminium chloride, their molecules are disintegrated with replacement of the complex groups by hydrogen. Thus, under these conditions, triphenylmethane, diphenylhexamethylbenzene, and durenene yield benzene.

Conversely, naphthalene gives isodinaphthyl together with its hydrides; benzene gives toluene and ethylbenzene together with diphenyl, and toluene gives xylene and ethyltoluene together with ditolyl. Thus there is a disintegration of a certain number of molecules of benzene with formation of methyl and ethyl groupings; whilst at the same time there is an interchange of hydrogen for phenyl, these changes being due to a concomitant hydrogenation on the one hand, and dehydrogenation on the other. According to the theory put forward by the authors in their experiments on the synthesis of hydrocarbons by means of aluminium chloride, there occurs a change of hydrogen in the hydrocarbon, and of chlorine in the aluminium chloride, thus:  $C_6H_6 + Al_2Cl_6 = Al_2Cl_5Ph + HCl$ . The decomposition of hydrocarbons described above may probably be explained by an analogous change, the compound  $Al_2Cl_5Ph$  yielding diphenyl and a lower chloride of aluminium, which is converted by hydrogen chloride into aluminium chloride and hydrogen. The separation of the paraffinoid groups may also be explained by the following reaction:  $PhMe + Al_2Cl_6 = PhAl_2Cl_5 + MeCl$ , the methyl chloride, however, does not appear as such, but undergoes a further transformation (compare Anschütz and Immendorf, this vol., p. 269, and Jacobsen, *ibid.*, p. 516).

V. H. V.

**Xylenes.** By A. COLSON (*Bull. Soc. Chim.*, 43, 6—8).—Monobromo-ortho- and -meta-xylenes,  $C_6H_4Me\cdot CH_2Br$ , are prepared in a manner exactly similar to that used for the preparation of the dibromo-derivatives (Abstr., 1884, 1000 and 1313). The ortho-compound boils at about 220° and the meta-compound at about 212°.

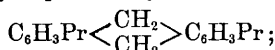
*Orthotolyl carbinol*,  $C_6H_4Me\cdot CH_2OH$ , is obtained by saponifying the corresponding bromide with a large excess of a solution of potassium carbonate, the alcohol being then separated from the aqueous solution

by saturation with potassium chloride or carbonate, when the alcohol rises to the surface; it is a white crystalline body, melts at  $34.2^{\circ}$ , is soluble in 100 parts of water at  $12^{\circ}$ , more soluble in hot water or in ether; it boils at  $216-217.5^{\circ}$ . When oxidised with permanganate, it yields orthotoluic acid.

*Metatolyl carbinol*, obtained in a similar manner, is a liquid boiling at  $216-217.5^{\circ}$  under a pressure of 758 mm.; it has a sp. gr. of 1.028 at  $12^{\circ}$ , and is soluble in 80 to 100 parts of water at  $12^{\circ}$ ; it is more soluble in hot water and in ether. It could not be solidified.

A. P.

**Action of Chlorine on Cymene.** By G. ERRERA (*Gazzetta*, **14**, 277—289).—As the author obtained a chlorocymene amongst the products of the chlorination of cymene from camphor (Abstr., 1884, 300), he has more carefully examined the constitution of this substance by a comparison of its reactions with those of the chlorocymene obtained directly by the action of hydrochloric acid on cymyl alcohol. It appears that the portion of the product of the chlorination of cymene, which boils between  $225-229^{\circ}$ , consists of three isomeric monochloro-derivatives. One of these is identical with the chlorocymene obtained from cymyl alcohol, and is readily oxidised into cumaldehyde and acids; its constitution is thus represented by the formula  $C_6H_5Pr \cdot CH_2Cl$ . It is converted slowly by boiling, but more rapidly in the presence of metallic chlorides into a hydrocarbon,  $C_{20}H_{24}$ , a yellowish solid melting at  $90^{\circ}$  and boiling above  $360^{\circ}$ ; its constitution is possibly expressed by the formula



with nitric acid, it yields a dinitro-derivative,  $C_{20}H_{24}(NO_2)_2$ . This chlorocymene is converted by alcoholic potash into the corresponding ethyl ether,  $C_6H_5Pr \cdot CH_2 \cdot OEt$ , a liquid boiling at  $227^{\circ}$ , and readily converted by metallic chlorides into the hydrocarbon  $C_{20}H_{24}$ .

Of the two other chlorocymenes obtained in the above reactions, both being probably represented by the formula  $C_6H_5Me \cdot C_3H_6Cl$ , one is converted by alcoholic potash into para-allylmethylbenzene,



a colourless liquid boiling at  $192^{\circ}$ , and transformed by contact with calcium chloride into a solid polymeride,  $nC_{10}H_{12}$ , which, by distillation, is reconverted into the primitive hydrocarbon. The third chlorocymene is unaltered by alcoholic potash.

V. H. V.

**Derivatives of Triphenylcarbinyl Bromide.** By W. ALLEN and A. KÖLLIKER (*Annalen*, **227**, 107—118).—When carefully dried ethylic acetosodacetate is suspended in ether and treated with triphenylcarbinyl bromide, a compound of the formula

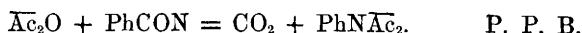


is obtained; it forms colourless crystals and melts at  $159.5-160.5^{\circ}$ . When saponified, it yields triphenylcarbinyl ethyl ether; this melts at  $83^{\circ}$ , and not at  $78^{\circ}$ , as stated by Hemilian (this Journal, 1875, 153).

A. J. G.

**Phenyl Cyanate.** By F. GUMPERT (*J. pr. Chem.* [2], **31**, 119—121).—Hofmann has shown that phenyl cyanate unites directly with primary alcohols to form urethanes; the author finds that it also unites with secondary and tertiary alcohols in a similar manner. Thus phenyl cyanate reacts with isopropyl alcohol to form *isopropyl phenylcarbamate*,  $\text{NHPh}\cdot\text{COOPr}^s$ , which crystallises from alcohol in white needles melting at  $90^\circ$ . With phenol it forms *phenyl phenylcarbamate*,  $\text{NHPh}\cdot\text{COOPh}$ , which crystallises in white needles melting at  $125^\circ$ . Phenyl cyanate does not, however, react with orthonitrophenol or picric acid. Phenyl cyanate unites directly with isatin when heated with it at  $100^\circ$ , forming a compound crystallising in yellow needles, and melting at  $180^\circ$  with decomposition into phenyl cyanate and isatin. This compound dissolves in caustic soda, and on adding an acid, a compound is precipitated which crystallises from alcohol in white needles, melting at  $187^\circ$ , and having the composition  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$ .

Phenyl cyanate, when heated with phosphoric chloride, gives phosphorus oxychloride and a chlorine-compound, which is not isocyanphenyl chloride,  $\text{NPhCCl}_2$ ; but when heated with zinc-dust yields methylaniline. Phenyl cyanate, dissolved in chloroform, is attacked by chlorine and bromine. When heated in sealed tubes at  $170^\circ$  with acetic anhydride, phenyl cyanate yields carbonic anhydride and acetanilide; the latter probably owes its formation to the action of acetic acid on diacetanilide, formed by the action of acetic anhydride on the phenyl cyanate, thus:—



**Action of Potassium Cyanide on Metadinitrobenzene.** By C. A. LOBBY DE BRUYN (*Rec. Trav. Chim.*, **2**, 205—237).—When metadinitrobenzene (1 mol.) is allowed to act on potassium cyanide (1 mol.) in alcoholic solution, potassium nitrite, a red colouring matter, and a colourless substance,  $\text{C}_6\text{H}_8\text{N}_2\text{O}_3$ , crystallising in slightly yellowish scales melting at  $137^\circ$ , are formed. The reaction takes place at the ordinary temperature, more readily on heating. If the potassium cyanide is dissolved in methyl alcohol instead of in ethyl alcohol, the colourless scales are replaced by a substance,  $\text{C}_8\text{H}_8\text{N}_2\text{O}_3$ , melting at  $171^\circ$ . The ethyl-derivative,  $\text{C}_8\text{H}_8\text{N}_2\text{O}_3$ , is soluble in cold chloroform, acetone, and ethyl acetate, and in boiling alcohol, acetic acid, nitric acid, and carbon bisulphide, very sparingly so in water. It sublimates with difficulty, and always with partial decomposition. It is decomposed on distillation. The methyl-derivative,  $\text{C}_6\text{H}_8\text{N}_2\text{O}_3$ , crystallises in long plant needles, and very closely resembles the ethyl-derivative. The colouring matter obtained when ethyl alcohol is employed in the above reaction, forms a shiny, black, amorphous mass, which contains potassium. It dissolves in alcohol to a red solution which dyes silk and wool; in water it dissolves to a brownish-red solution. That obtained in the methyl alcohol reaction gives a purer coloured alcoholic solution.

When heated with concentrated hydrochloric acid in closed tubes at  $160$ — $170^\circ$ , both compounds yield metanitrophenol. When heated with baryta-water these compounds yield small quantities of crystalline products having the formulæ  $\text{C}_8\text{H}_8\text{N}_2\text{O}_4$  and  $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_4$ .

respectively. The principal products are, however, two barium derivatives, which have not yet been obtained in a pure state.

When a solution of the methyl-derivative,  $C_8H_8N_2O_3$ , in methyl alcohol is heated with potash, a compound,  $C_9H_9NO_2$ , is produced, which crystallises in prismatic needles melting at  $118^\circ$ , and is soluble in alcohol and chloroform; it boils at about  $310^\circ$ . Potassium nitrite is formed in this reaction, so that the reaction would appear to consist of a displacement of  $NO_2$  by  $CH_3$ . When heated with hydrochloric acid at  $170^\circ$  this compound yields resorcinol. When heated with baryta, or fused with potash, a compound of the composition of a dihydroxybenzoic acid is formed. This acid appears to be the  $\beta$ -meta-dihydroxybenzoic acid of Senhofer and Brunner (Abstr., 1881, 265), which Tiemann and Parrisius (Abstr., 1881, 739), have proved to have the constitution  $[COOH : OH : OH = 1 : 2 : 6]$ . With strong nitric acid, this compound yields a substance,  $C_9H_8N_2O_4$ , crystallising in needles which melt at  $111^\circ$ .

Under similar conditions, methyl alcohol and potash yield with the ethyl-derivative a substance,  $C_{10}H_{11}NO_2$ , which crystallises in prismatic needles or large plates melting at  $66^\circ$ , and is soluble in benzene, chloroform, acetone, &c. Ethyl alcohol, potash, and the methyl-derivative appear to yield the same compound.

Ethyl alcohol, potash, and the ethyl-derivative form a compound,  $C_{11}H_{13}NO_2$ , which crystallises in aggregated needles melting at  $122^\circ$ , and easily soluble in benzene, chloroform, acetone, and carbon bisulphide. It is noticeable that the compounds containing two similar radicles have much higher melting points ( $118^\circ$  and  $122^\circ$ ) than that containing two different radicles ( $66^\circ$ ). The two former compounds are also less soluble than the latter. All three (or four) compounds boil at about  $310^\circ$  under partial decomposition.

From a careful consideration of all the reactions just described, the author believes the two crystalline derivatives to be *methoxy-* and *ethoxy-nitrobenzenenitriles*,  $NO_2 \cdot C_6H_3(OR) \cdot CN$ , and of the constitution  $[CN : NO_2 : OR = 1 : 2 : 6]$ .

L. T. T.

**Displacement of the  $NO_2$  Group by an Oxyalkyl-group.** By C. A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 2, 235—237).—The author calls attention to the examples in the preceding Abstract of the replacement of a nitro-group by an oxyalkyl-group when the nitro-compound is treated with potash and an alcohol. Nitro-compounds when treated with alcoholic potash usually yield azo-derivatives, but in all cases potassium nitrite is formed at the same time, and the author finds that ortho-dinitrobenzene yields orthonitranisole with potash and methyl alcohol, and ethyl orthonitrophenyl ether with potash and ethyl alcohol.

L. T. T.

**Action of Potassium Cyanide on Ortho- and Para-dinitrobenzene, and Separation of Orthodinitrobenzene from its Isomerides.** By C. A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 2, 238—240).—When heated with an alcoholic solution of potassium cyanide, orthodinitrobenzene yields only a trace of potassium nitrite, almost the whole of the orthodinitrobenzene remaining unchanged. Potassium



cyanide does not act on paradinitrobenzene at ordinary temperatures, but if the mixture is boiled, potassium nitrite and a substance of an aromatic odour are formed. The latter substance is crystalline and melts at 59°. It is therefore not formed by the displacement of one of the  $\text{NO}_2$  groups by  $\text{CN}$ , as paranitrocyanobenzene melts at 147°. The author did not obtain sufficient substance for further investigation.

The inactivity of orthodinitrobenzene towards potassium cyanide may be utilised to separate it from its isomerides. The mixture is digested with an alcoholic solution of potassium cyanide and, when all action has ceased, evaporated to dryness. The residue is dissolved in nitric acid of sp. gr. 1.35, the solution poured into water, and the precipitate which forms is filtered off and distilled with steam: orthodinitrobenzene then passes over in a pure state.

L. T. T.

**Action of Hydrogen Peroxide on the Phenols.** By MARTINON (*Bull. Soc. Chim.*, **43**, 155—158).—If during the gradual addition of an aqueous solution of hydrogen peroxide in the cold to pure phenol, the solution is kept neutral or only slightly acid, and the temperature afterwards raised to 80—90°, the mixture cooled, filtered, and the clear solution treated with acetate of lead, a precipitate of the lead compound of catechol is thrown down, from which pure catechol may be obtained. Quinol is obtained by extracting with ether the aqueous solution filtered from the lead salt. Quinone is also formed in the reaction. Resorcinol yields analogous reactions, but not so readily.

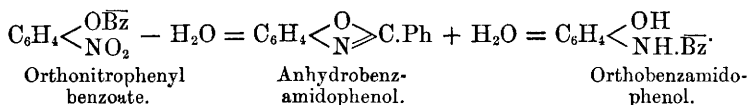
A. P.

**Bromoxytribromophenol.** By E. WERNER (*Compt. rend.*, **100**, 799—801).—By the action of bromine in excess on the phenols, four atoms of hydrogen are replaced by the bromine, of which three hydrogen-atoms are in the hydrocarbon, and one in the hydroxyl-group. Thus from phenol there is formed bromoxytribromophenol,  $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{OBr}$ , crystallising in scales; this substance is gradually decomposed by water; it liberates iodine from potassium iodide. As a mean of three different experiments, evolution of heat of 73.7 cal. resulted from the equation  $\text{C}_6\text{H}_6\text{O} + (4\text{Br}_2 + n\text{Br}) \text{ diss.} = (4\text{HBr} + n\text{Br}) \text{ diss.} + \text{C}_6\text{H}_2\text{Br}_4\text{O(sol.)} = + 73.77 \text{ cal.}$  Comparing this value with those of Berthelot and the author for the substitution of one to three atoms of hydrogen by bromine, it is found for each of the three phenylic hydrogen-atoms substituted 20—26 cal. are evolved, but for the fourth, or oxylic, only 5.3 cal., a result in accordance with the unstable character of the resultant bromoxybromophenol.

V. H. V.

**Migrations in Benzene Ortho-di-derivatives.** By W. BÖTTCHER (*Chem. Centr.*, 1884, 898—899).—The author has repeated Hübner's experiments on the reduction of orthonitrophenyl benzoate (*Abstr.*, 1882, 506) with tin and hydrochloric acid. In his first experiment, he obtained anhydrobenzamidophenol exactly as described by Hübner. In another, where he precipitated the tin from the hot alcoholic solution, he obtained a benzamidophenol,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{Bz}$ , melting at 167°, as well as the anhydro-derivative. The benzamido-

phenol is derived from the anhydro-compound first formed by the action of the hydrochloric acid liberated by the hydrogen sulphide. The phenol is converted by distillation into the anhydro-compound, from which it may be again obtained by digestion with hydrochloric acid. Thus the benzoyl-group has migrated from the oxygen-atom in ortho-nitrophenyl benzoate to the nitrogen-atom in benzamidophenol. It is undoubtedly due to the formation of the intermediate anhydro-compound that this transposition is possible, thus :—



An attempt to produce a similar migration in the case of ortho-nitrophenyl acetate proved fruitless. But  $\alpha$ -nitro- $\beta$ -naphthyl benzoate,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{O}\overline{\text{Bz}}$  (melting at 142), yielded, on reduction with glacial acetic acid and zinc-dust, a mixture of the anhydro-base, *benzenyl- $\alpha$ -amido- $\beta$ -naphthol*,  $\text{C}_{10}\text{H}_6\text{<}\begin{smallmatrix}\text{O} \\ \text{N}\end{smallmatrix}\text{>CPh}$  (colourless needles melting at 136°), and  *$\alpha$ -benzamido- $\beta$ -naphthol*,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\overline{\text{Bz}}$ , small colourless scales, melting at 245°. The benzamidonaphthol is converted into the anhydro-base by careful heating. The solutions of these compounds show a blue fluorescence.

$\alpha$ -Nitro- $\beta$ -naphthyl acetate, on reduction, yields a mixture of *ethenyl-amidonaphthol*,  $\text{C}_{10}\text{H}_6\text{<}\begin{smallmatrix}\text{O} \\ \text{N}\end{smallmatrix}\text{>CMe}$ , an oil having the odour of anise, and  *$\alpha$ -acetamido- $\beta$ -naphthol*,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\overline{\text{Ac}}$  (scales melting at 225°). The acetamido-naphthol yields the anhydro-base by sublimation, but is re-formed when the aqueous solution of the sulphate of that base is heated.

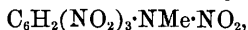
L. T. T.

**Derivatives of Carvacrol.** By POLECK and LUSTIG (*Chem. Centr.*, 1884, 787—788).—The sodium-derivative of carvacrol was obtained by the action of sodium on a solution of carvacrol in light petroleum. It is a white amorphous powder, which readily absorbs water and carbonic anhydride. When heated at 100° with ethyl iodide, it yields an ethyl ether which is a mobile oil, lighter than water, and boils at 235°. When treated with acetic or benzoic chloride, carvacrol yields the acetate or benzoate. Both of these salts are thick oils, heavier than water. When subjected to Tiemann and Reimer's reaction with potash and chloroform, carvacrol yields an oil of the formula  $\text{OH}\cdot\text{C}_{10}\text{H}_{12}\cdot\text{COH}$ , which possesses the properties of an aldehyde. When exposed to the air, this aldehyde absorbs oxygen, and is converted into the corresponding acid,  $\text{OH}\cdot\text{C}_{10}\text{H}_{12}\cdot\text{COOH}$ , which crystallises in small silky needles; this acid is not identical with Kekulé's carvacrotinic acid, obtained by the action of sodium on carvacrol in the presence of carbonic anhydride. The melting point of the latter acid is 136°, that of the authors' acid 80°. Kekulé's acid gives a violet, the other a green coloration with ferric chloride. Both isomeric acids are sparingly soluble in water, easily so in alcohol and ether.

The aldehyde described above, when treated with hydroxylamine, yields an *acetoxime*, which crystallises in small needles.

L. T. T.

**Non-existence of Pentanitrodimethylaniline.** By P. VAN ROMBURGH (*Rec. Trav. Chim.*, **2**, 304—307).—Michler and Salathé (Abstr., 1880, 108) and Michler and K. Meyer (Abstr., 1880, 108) have described a pentanitrodimethylaniline obtained by the oxidation respectively of naphthylidimethamidophenylsulphone and diphenyldimethamidosulphone by means of fuming nitric acid. As this substance appeared to resemble trinitromethylnitraniline,



lately obtained by the author (*Rec. Trav. Chim.*, **2**, 108), he has repeated Michler and Meyer's work. He finds the substance in question (and therefore also that obtained by Michler and Salathé) is trinitromethylnitraniline, and not pentanitrodimethylaniline. It forms yellow crystals melting at 127°.

L. T. T.

**Derivatives of Amidoazobenzene.** By G. BERJU (*Chem. Centr.*, 1884, 871).—*Acetyl-amidoazobenzene*,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , prepared from amidoazobenzene and acetic anhydride, forms yellow needles melting at 143°. When treated with methyl iodide, amidoazobenzene yields *monomethamidoazobenzene*,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}$ , crystallising in red needles, melting at 108°, and yielding a hydrochloride in the form of violet needles. The *acetyl-derivative* forms silky needles, melting at 139°. *Dimethamidoazobenzene* may be obtained by the action of methyl iodide on the monomethyl-derivative, or still better by acting on diazobenzene with dimethylaniline. It yields orange needles melting at 117°. When heated with methyl iodide in closed tubes at 100° it forms azobenzenetrimethylammonium iodide,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$ , which crystallises in flesh-coloured flakes, melting at 273—274°. It is not decomposed by potash or soda.

When benzaldehyde is gently heated with amidoazobenzene, it yields *benzylideneamidoazobenzene*,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{CHPh}$ , which crystallises in orange needles, melting at 128°. Hydrochloric acid breaks it up again into its constituents. A dilute alcoholic solution of bromine converts amidoazobenzene into dibromamidoazobenzene,  $\text{C}_{12}\text{H}_9\text{N}_3\text{Br}_2$ , crystallising in yellow needles, and melting at 152°. When reduced with tin and hydrochloric acid, amidoazobenzene yields aniline and paraphenylenediamine. With a solution of phosgene gas in benzene, amidoazobenzene yields *carbamidoazobenzene*,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph})_2$ , which forms microscopic yellow flakes, melting at 270°, but is not capable of forming salts. With an alcoholic solution of phenyl thiocarbimide, amidoazobenzene yields yellow microscopic scales of amidazobenzene-phenylthiocarbamide,  $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$  (m. p. 270°), together with thiocarbamidoazobenzene,  $\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph})_2$ , melting at 199°. The latter compound loses its sulphur when heated with mercuric oxide and yields carbamidoazobenzene.

L. T. T.

**Reduction of Isodinitrobenzene.** By GOLOUBEFF (*Bull. Soc. Chim.*, **43**, 128).—By acting on isodinitrobenzene with tin and an

alcoholic solution of hydrogen chloride, a crystalline substance having the formula  $C_{14}H_{10}N_2$  is obtained; it is soluble in alcohol and in boiling acetic acid; when this compound is heated with alcoholic potash, an amorphous substance is formed. The compound,  $C_{14}H_{10}N_2$ , does not combine with acids, but when heated with a slight excess of benzoic chloride at  $100^\circ$ , hydrogen chloride is disengaged, and a crystalline compound,  $C_{14}H_8N_2\overline{Bz}_2$ , is formed, melting at  $239.5$ — $240.5^\circ$ , which on boiling with alcoholic soda is decomposed, benzoic acid and the compound  $C_{14}H_{10}N_2$  being formed. The benzoic compound dissolves in benzene, forming a very unstable additive compound,



**Derivatives of Orthamidobenzamide.** By A. WEDDIGE (*J. pr. Chem.* [2], 31, 124—126).—*Acetyl orthamidobenzamide*,



is formed by the action of acetic anhydride on orthamidobenzamide, it crystallises from alcohol in thick shining colourless needles; it melts at  $170$ — $171^\circ$ , and at the same time is resolved into water and *anhydroacetyl orthamidobenzamide*,  $C_8H_8N_2O$ , which crystallises from alcohol in yellow, silky, lustrous needles melting at  $228^\circ$ . The anhydride forms salts with acids, the hydrochloride crystallises in long yellow needles. It dissolves in caustic soda, forming a yellow solution, from which the sodium salt is obtained in small needles.

With formic acid, orthamidobenzamide yields a formyl-derivative, melting at  $123^\circ$ , converted by heat into the anhydride melting at  $209$ — $210^\circ$ .  
P. P. B.

**Azophenylacetic Acid.** By WITTENBERG (*Bull. Soc. Chim.*, 43, 111).—*Azophenylacetic acid*,  $N_2(C_6H_4 \cdot CH_2 \cdot COOH)_2$ , is prepared by reducing symmetrical nitrophenylacetic acid (m. p.  $151^\circ$ ) by means of sodium amalgam; it resembles other azo-acids, is insoluble in hot water, slightly more soluble in hot alcohol (100 grams of alcohol dissolve 0.375 gram), insoluble in ether and in benzene, and only very slightly soluble in chloroform. It is decomposed without melting at  $300^\circ$ . The potassium, sodium, silver, and barium salts were prepared.

A. P.

**Cinnamic and Hydrocinnamic Acids, and Paranitrobenzaldehyde.** By M. HERZBERG (*Chem. Centr.*, 1884, 35).—*Chlorocinnamic acid*,  $C_6H_4Cl \cdot C_2H_2 \cdot COOH$ , prepared from orthodiazocinnamic acid, melts at  $200^\circ$ , and when treated with phosphorus and hydriodic acid is converted into *ortho-chlorophenylpropionic acid*, melting at  $96.5^\circ$ . By heating orthodiazocinnamic acid nitrate with hydriodic acid, *orthiodocinnamic acid*, melting at  $212$ — $214^\circ$ , may be obtained, and from this iodophenylpropionic acid melting at  $102$ — $103^\circ$ , which, however, by too long exposure to the action of hydriodic acid and phosphorus is converted into phenylpropionic acid.

From metanitrocinnamic acid (obtained by heating together meta-nitrobenzaldehyde, acetic anhydride and sodium acetate) metadiazocinnamic acid has been prepared, and from this, by similar methods to those used in preparing the ortho-compounds, the author has

obtained *metachlorocinnamic acid*,  $C_6H_4Cl \cdot C_2H_2 \cdot COOH$ , melting at  $167^\circ$ , *metachlorophenylpropionic acid*, melting at  $78^\circ$ , *metiodocinnamic acid*, melting at  $182^\circ$ , and *metiodophenylpropionic acid*, melting at  $65-66^\circ$ , this latter containing traces of phenylpropionic acid. The following para-compounds were also prepared: *parachlorocinnamic acid*, melting at  $240-242^\circ$ , *para-chlorophenylpropionic acid*, melting at  $124^\circ$ , *paraiodocinnamic acid*, melting at  $255^\circ$ , and *paraiodophenylpropionic acid*, melting at  $140-141^\circ$ .

Para-acetamidocinnamic acid, melting at  $259-260^\circ$ , is formed from paramidocinnamic acid and anhydrous acetic acid; when acted on by fuming nitric acid, it yields *dinitropara-acetamidocinnamene*,



melting at  $211-212^\circ$ . By acting on acetamidocinnamic acid with fuming nitric acid at a very low temperature, the mononitro-acid is formed from which, by the action of sodium hydroxide, metanitro-paramidocinnamic acid, melting at  $224.5^\circ$ , may be obtained. By treating this substance with an alkaline solution of stannous oxide, it is converted into metaparadiamidocinnamic acid, melting at  $167-168^\circ$ . Bromine converts para-acetamidocinnamic acid into bromacetamidocinnamene, melting at  $182.5^\circ$ .

*Paranitrobenzaldoxime*,  $NO_2 \cdot C_6H_4 \cdot CH : NOH$  [1:4], melting at  $128.5^\circ$ , is obtained by the action of hydroxylamine on paranitrobenzaldehyde. When treated with ammonium sulphide, it is converted into paramidobenzaldoxime melting at  $124.5^\circ$ . On the addition of an excess of acid, it yields a red jelly or dark red needles which reflect a blue light. This appearance is characteristic of the para-compounds, whilst the isomeric ortho- and meta-compounds yield colourless salts. The red compound contains paramidobenzaldehyde, which crystallises in yellow needles and gives a red salt with hydrochloric acid. Para-acetamidobenzaldehyde and paracetamidobenzaldoxime, melting at  $205-206^\circ$ , are finally described.

A. P.

**Nitration in the Side-chains of Aromatic Compounds.** By H. ERDMANN (*Chem. Centr.*, 1884, 809).—By the action of nitromethane on benzaldehyde, Priebis has obtained phenylnitroethylene identical with that which the author prepared (*Abstr.*, 1884, 906) by acting on phenylisocrotonic acid with fuming nitric acid. By the nitration of ethyl paranitrocinnamate, Friedländer and Mähly (*Ber.*, 16, 850) obtained an ethyl dinitrocinnamate in which the second nitro-group was also in the side-chain. The free acid evolved carbonic anhydride when heated, and yielded paranitrophenylnitroethylene. By passing nitrous acid into a solution of cinnamic acid in dry ether, and distilling the product with steam, the author obtained phenylnitroethylene. The homologues of cinnamic acid react in a similar manner. On reduction, phenylnitroethylene evolves ammonia, and all attempts to obtain the hypothetical cinnoline by the reduction of nitrophenylnitroethylene proved unavailing.

L. T. T.

**Formation of Phenylangelic and Phenylmethacrylic Acids: Behaviour of Ethylphenyllactic Acid.** By F. L. SLOCUM

(*Annalen*, **227**, 53—61).—The author has already shown (Abstr., 1883, 112) that phenylangelic acid is alone formed by the action of benzaldehyde on a mixture of acetic anhydride and sodium butyrate at 100°. A mixture of benzaldehyde, acetic anhydride, and sodium propionate when heated at 100°, yields pure phenylmethacrylic acid. Phenyllactic acid is not formed by heating together a mixture of benzaldehyde, acetic anhydride, and sodium acetate at 125°, but cinnamic acid is alone obtained. The non-formation of phenyllactic acid is explained as probably due to the fact that in the presence of acetic anhydride, acetylphenyllactic acid is formed and suffers decomposition into cinnamic acid at 115—120°.

A. J. G.

**Phenylhydroxypivalic Acid.** By P. OTT (*Annalen*, **227**, 61—79).—Phenylhydroxypivalic acid was prepared by Fittig and Jayne (Abstr., 1883, 471) by heating a mixture of isobutyric anhydride, sodium isobutyrate, and benzaldehyde. It is not, however, formed directly, but is a decomposition product of *phenylisobutyroxypivalic anhydride*. This substance was only obtained in an impure state as an oil; when boiled with water, it yields the corresponding acid. *Phenylbutyroxypivalic acid*,  $C_4H_7O \cdot O \cdot CHPh \cdot CMe_2 \cdot COOH$ , crystallises in needles, melts at 65°, is sparingly soluble in water, but readily in most other solvents. The *barium* salt,  $(C_{15}H_{19}O_4)_2Ba + 2H_2O$ , the *calcium* salt,  $(C_{15}H_{19}O_4)_2Ca + 2H_2O$ , and the *silver* salt,  $C_{15}H_{19}O_4Ag$ , are described. When boiled with baryta-water, it yields isobutyric and phenylhydroxypivalic acids. The acid can be obtained by the action of isobutyric anhydride on phenylhydroxypivalic acid.

*Phenylacetoxypivalic anhydride*,  $C_{25}H_{30}O_7$ , is prepared by heating a mixture of acetic anhydride and the hydroxy-acid at 100°. It crystallises in prisms belonging to the rhombic or monosymmetric system. When heated with water or alkalis, it is more or less completely resolved into acetic and phenylhydroxypivalic acids.

*Phenylacetoxypivalic acid*,  $\overline{Ac}O \cdot CHPh \cdot CMe_2 \cdot COOH$ , is formed at the same time as the anhydride; it crystallises in monosymmetric prisms,  $a : b : c = 1.374 : 1 : 0.8243$ ,  $\beta = 64^\circ 34'$ ; observed faces  $\infty P$ ,  $0P$ ,  $P\infty$ ,  $-P$ ,  $+P$ , and  $\infty P\infty$ . It melts at 137°, and is sparingly soluble in water. The barium and calcium salts are described.

When a mixture of benzaldehyde, sodium isobutyrate, and acetic anhydride is heated at 100°, phenylacetoxypivalic anhydride is formed, together with a small quantity of the corresponding butyroxycoumarin compound.

A. J. G.

**Perkin's Reaction.** By R. FITTIG (*Annalen*, **227**, 48—53).—The author regards the facts brought forward in the preceding Abstracts as confirmatory of the views he has already published (Abstr., 1883, 1122) as to the nature of the changes occurring in Perkin's method for the synthesis of acids of the acrylic series.

A. J. G.

**Hydroxybenzaldehyde and Coumaric Acid.** By R. LUDWIG (*Chem. Centr.*, 1884, 35).—Metamidobenzaldehyde is obtained by the reduction of metanitrobenzaldehyde, as a yellow amorphous substance; sodium nitrite and hydrochloric acid convert it into metadiazocoumaric acid.

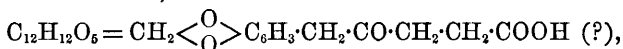
benzaldehyde, which when heated loses the whole of its nitrogen, meta-hydroxybenzaldehyde, melting at  $104^{\circ}$ , being formed. From this substance, acetometahydroxybenzaldehyde, melting at  $263^{\circ}$ , and methyl-metahydroxybenzaldehyde may be prepared. When fused with sodium acetate and acetic anhydride, metahydroxybenzaldehyde yields acetometacoumaric acid melting at  $151^{\circ}$ , and on heating this with potassium hydroxide it is converted into the potassium salt of metacoumaric acid; this acid melts at  $191^{\circ}$ , and is reduced to hydroxymetacoumaric acid, melting at  $111^{\circ}$ , by means of sodium amalgam (compare Braunstein *Inaug. Diss.*, Zurich, 1876). Methylmetacoumaric acid melting at  $115^{\circ}$ , and from this hydromethylmetacoumaric acid melting at  $51^{\circ}$ , may be obtained by a similar process from the methylmetahydroxybenzaldehyde.

Metahydroxybenzaldehyde when nitrated yields  $\beta$ -nitrometahydroxybenzaldehyde melting at  $166^{\circ}$ ,  $\alpha$ -nitrometahydroxybenzaldehyde melting at  $128^{\circ}$ , and  $\gamma$ -nitrometabenzaldehyde melting at  $138^{\circ}$ .

$\alpha$ - and  $\beta$ -Nitrometahydroxybenzaldehydes, melting at  $107^{\circ}$  and  $82-83^{\circ}$  respectively, are described. Methylmetahydroxybenzaldehyde when nitrated yields  $\alpha$ - and  $\beta$ -dinitromethylmetahydroxybenzaldehydes melting at  $110^{\circ}$  and  $155^{\circ}$  respectively. A. P.

**$\alpha$ - and  $\beta$ -Hydropiperic Acids.** By L. WEINSTEIN (*Annalen*, **227**, 31—48).—The two hydropiperic acids obtained by the treatment of piperic acid with sodium amalgam, are distinguished by the peculiar facts that the  $\alpha$ -acid forms an additive product (dibromopiperhydronic acid) with bromine, but does not unite with nascent hydrogen, whilst on the contrary the  $\beta$ -acid unites with two atoms of hydrogen, but yields a substitution-derivative (bromo- $\beta$ -hydropiperic acid) instead of an additive compound with bromine (Buri, *Abstr.*, 1883, 485). The present investigation of these bromine-derivatives was undertaken in the hope of throwing some light on the constitution of the isomeric hydro-acids.

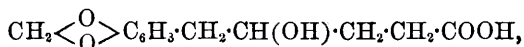
*Piperoketonic acid,*



is formed by the action of sodium carbonate on dibromopiperhydronic acid. It crystallises in silky interlaced needles, melts at  $84^{\circ}$ , and is readily soluble in alcohol, ether, chloroform, and benzene. This acid does not seem to be formed directly from the bromo-acid, an oily lactone-like substance being first produced. The *calcium* salt,  $(C_{12}H_{11}O_5)_2Ca$ , and the *silver* salt,  $C_{12}H_{11}O_5Ag$ , are described. The *ethyl* salt forms a pale yellow oil; it does not yield an acetyl-derivative.

*Piperohydrolactone*,  $C_{12}H_{12}O_4 = CH_2 < \overset{O}{\underset{\text{O}}{\parallel}} > C_6H_5 \cdot CH_2 < \overset{CH \cdot CH_2}{\underset{O-CO}{\parallel}} > (?)$ ,

prepared by the action of sodium amalgam on piperoketonic acid, forms a clear, yellow oil; when treated with bases it is converted into the salts of *hydroxypiperhydronic acid*. The free acid,



forms lustrous, colourless crystals, melts at  $95^{\circ}$ , is readily soluble in alcohol and ether, moderately soluble in hot water. It is readily decomposed into water and the lactone. The silver and barium salts are described.

Bromo- $\beta$ -hydropiperic acid is not decomposed by boiling with aqueous sodium carbonate. This would seem to point to the bromine-atom being attached to the benzene ring, a view confirmed by the results of oxidation with alkaline permanganate, when bromopiperonal, bromopiperonylic acid, and a new acid, *bromopiperopropionic acid*, are formed. This last acid,  $\text{CH}_2 < \overset{\text{O}}{\text{O}} > \text{C}_6\text{H}_4\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , crystallises in monosymmetric forms, melts at  $139\cdot6^{\circ}$ , is sparingly soluble in water, moderately soluble in alcohol and ether. The calcium salt,  $(\text{C}_{10}\text{H}_8\text{BrO}_4)_2\text{Ca}$ , crystallises in long, thin needles.

The author considers that these results point to the constitutions  $\text{CH}_2 < \overset{\text{O}}{\text{O}} > \text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$  for  $\alpha$ -hydropiperic acid, and  $\text{CH}_2 < \overset{\text{O}}{\text{O}} > \text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{COOH}$  for  $\beta$ -hydropiperic acid.

A. J. G.

**Unsymmetrical Metadinitrobenzenesulphonic Acid.** By C. WILLGERODT and P. MOHL (*Chem. Centr.*, 1884, 809—810).—This acid,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{SO}_3\text{H}$  [ $\text{SO}_3\text{H}:\text{NO}_2:\text{NO}_2 = 1:2:4$ ], is obtained by heating  $\alpha$ -dinitrophenyl bisulphide with fuming nitric acid; it crystallises in slightly yellowish prisms melting at  $106\text{--}108^{\circ}$ , and easily soluble in water, alcohol, and acetone, sparingly so in ether and acetic acid. Its sulphochloride is obtained by acting on the acid with phosphoric chloride. This acid is not identical with either of the dinitrobenzenesulphonic acids obtained by Limpricht.

L. T. T.

**Chemical Constitution of Isatin.** By H. KOLBE (*J. pr. Chem.* [2], 30, 467—483).—Isatin is best oxidised by a solution of chromic acid in glacial acetic acid; the oxidising mixture is slowly added, care being taken that the temperature does not rise above  $50^{\circ}$ ; after remaining for 12 hours in a flask surrounded by cold water, the temperature of the mixture is raised to  $50^{\circ}$ , and kept at that point for some hours; finally it is further heated to  $60^{\circ}$ , when the isatoic acid separates as a yellow powder.

*Isatoic acid* crystallises from hot acetone in hard, yellow prisms, and melts at  $230^{\circ}$ . The author regards its constitution as being  $\text{CO}\cdot\text{C}_6\text{H}_4\text{N}\cdot\text{COOH}$ , in which the nitrogen plays the part of a monovalent atom replacing one atom of hydrogen. Heated with water alone, it yields carbonic anhydride and orthamidobenzoic acid. With hydrochloric acid, the corresponding chloride is formed. Sulphuric and dilute nitric acids react on isatoic acid in a similar manner. Hydrogen chloride passed through an alcoholic solution of this body gives the hydrochloride of ethyl orthamidobenzoate, which melts at  $170^{\circ}$ , and is decomposed by water, yielding ethyl orthamidobenzoate, boiling at  $260^{\circ}$ .

Bases decompose isatoic acid also, with elimination of carbonic anhydride. As this takes place in the cold, it has not been found



possible to prepare salts of isatoic acid. Aqueous ammonia dissolves it with ease, forming ammonium carbonate and orthamidobenzamide, a body which crystallises from chloroform in large white plates, and melts at  $108^{\circ}$ , distilling with partial decomposition at  $300^{\circ}$ . Aniline acts in a similar manner, yielding the corresponding anilide, which crystallises from benzene in colourless needles melting at  $130^{\circ}$ .

Concentrated nitric acid dissolves isatoic acid, the mixture solidifying after a few hours to a mass of crystals, from which *nitroisatoic acid* is obtained by repeated crystallisation from equal quantities of absolute alcohol and acetone. It forms colourless shining crystals, melting with decomposition between  $220^{\circ}$  and  $230^{\circ}$ , and is more stable than isatoic acid. Heated with hydrochloric acid, it yields a strong acid which in its properties agrees with the metanitro-orthamidobenzoic acid described by Griess. The same compound is obtained from nitroisatoic acid by heating it with water alone. Aqueous ammonia yields the corresponding amide, a substance which crystallises from acetone in yellow needles, and decomposes between  $200^{\circ}$  and  $210^{\circ}$ .

By the reduction of nitroisatoic acid with tin and hydrochloric acid, the hydrochloride of  $\alpha$ -diamidobenzoic acid is formed, carbonic anhydride being evolved. Sulphuric acid yields the corresponding sulphate in hard transparent prisms soluble in water.

When isatoic acid, suspended in water at  $70^{\circ}$ , is treated with nitrous acid, nitrogen and carbonic anhydride are evolved, and the filtered solution yields on evaporation crystals of  $\alpha$ -nitrosalicylic acid.

The author concludes by stating that the formula proposed by him for isatin,  $C_6H_4NCO \cdot COH$ , in which one of the five phenyl hydrogen atoms is replaced by one atom of monovalent nitrogen, is most in accord with, and gives the simplest explanation of, the facts above adduced as to the behaviour of this body and its derivatives.

J. K. C.

**Isatoic Acid.** By E. v. MEYER (*J. pr. Chem.* [2], 30, 484—487).—Anthranilcarboxylic acid, described by Friedländer and Wleügel (*Ber.*, 16, 2227), has the same composition as isatoic acid, and agrees with it in several of its properties. The author gives a brief account of experiments in progress to establish the identity or otherwise of these two substances.

Treated with chromic acid or potassium permanganate, isatoic acid undergoes partial decomposition; a product is, however, obtained in colourless prisms, which has the same constitution as isatoic acid, and is identical with anthranilcarboxylic acid, being probably an isomeride of the former.

Ethyl and methyl alcohol, heated with isatoic acid to  $140^{\circ}$ , yield the corresponding ethers of carboxylanthranilic acid. With benzoic chloride, in the same manner, benzoylanthranil is formed.

J. K. C.

**Paramethylisatoic Acid and its Derivatives.** By W. PANAOVIC (*J. pr. Chem.* [2], 31, 122—124).—This acid is formed by oxidising paramethylisatin, dissolved in acetic acid, with chromic acid. The methylisatin used was prepared by P. J. Meyer's method

(*Ber.*, 16, 2261). *Methylisatoic acid*,  $C_9H_7NO_3$ , is sparingly soluble in water, easily soluble in boiling alcohol, from which it separates in rhombic tablets. It decomposes at  $245^\circ$ , is unaltered when heated with dilute hydrochloric acid, but by the concentrated acid is resolved into carbonic anhydride and a compound melting at  $207^\circ$ . With aqueous ammonia, methylisatoic acid yields carbonic anhydride and a crystalline compound melting at  $178^\circ$ ; it also reacts with aniline, forming a compound melting at  $243^\circ$ . Nitric acid converts methylisatoic acid into a compound crystallising in rhombic prisms, and melting at  $231^\circ$ .  
P. P. B.

**Phenols of High Boiling Point contained in Coal-tar.** By K. E. SCHULZE (*Annalen*, 227, 143—153).—The author has isolated  $\alpha$ - and  $\beta$ -naphthol from the high boiling fractions of coal-tar.

A. J. G.

**$\alpha$ -Naphthaquinone and its Derivatives.** By MILLER (*Bull. Soc. Chim.*, 43, 125—126).—*Dibromonaphthaquinone* is obtained by the action of bromine, in the presence of iodine, on  $\alpha$ -naphthaquinone. It forms long, yellow needles, melts at  $218^\circ$ , is slightly soluble at the ordinary temperature in alcohol, ether, petroleum, and acetic acid. It appears to be quite unaffected by the most active oxidising agents, as it even crystallises without change from solution in concentrated boiling nitric acid. By acting on its alcoholic solution with aniline, *bromonaphthanilide* is obtained, crystallising in red scales; it melts at  $194^\circ$ , and is slightly soluble in alcohol, ether, and acetic acid.

It is resolved into aniline and bromhydroxy- $\alpha$ -naphthaquinone when heated with an aqueous solution of the alkaline carbonates or hydroxides, or dilute sulphuric acid.

Bromhydroxynaphthaquinone crystallises in yellow prisms, and melts at  $201$ — $202^\circ$ , and has the properties of an acid. By treating bromhydroxynaphthaquinone with nitrous acid, phthalic acid is obtained; its constitution is therefore  $C_{10}H_4BrO_2 \cdot OH$  [O : Br : OH : O = 1 : 2 : 3 : 4].  
A. P.

**Naphthalfluoresceïn and Naphthaleosin.** By A. TERRISSE (*Annalen*, 227, 133—143).—*Naphthalfluoresceïn*,  $C_{24}H_{14}O_5$ , is prepared by heating naphthalic anhydride (1 part) with resorcinol (3 parts) for three hours at  $260$ — $270^\circ$ . In the presence of zinc chloride, the reaction can be completed in  $1\frac{1}{2}$  hours at  $215^\circ$ . It crystallises in pale yellow rhombic prisms, and melts at  $308^\circ$ . It dissolves in alkalis to a red-brown, or in dilute solution, reddish-yellow liquid, showing a strong green fluorescence. When boiled with acetic anhydride, it yields a *monacetate*,  $C_{24}H_{13}O_5\bar{Ac} + H_2O$ , crystallising in colourless needles; the hydrated compound melts at  $120^\circ$ , when anhydrous at  $191^\circ$ . It is readily decomposed by alkalis. Its behaviour with acetic anhydride thus differs from that of ordinary fluoresceïn which yields a diacetate. The presence of two hydroxyl-groups in the compound is, however, shown by heating it with phosphoric chloride, when a *dichloride*,  $C_{24}H_{12}Cl_2O_3$ , is formed, crystallising in pale yellow plates melting at  $283^\circ$ , and readily soluble in chloroform, acetone, and glacial acetic acid.

*Naphthalfluorescein* appears to be formed when naphthalfluoresceïn is treated with zinc-dust in alkaline solution, the liquid being decolorised, but the product reoxidises to the fluoresceïn with such readiness that its isolation could not be effected.

*Naphthaleosin* (*tetrabromonaphthalfluoresceïn*),  $C_{24}H_{10}Br_4O_5$ , obtained by adding bromine to an alcoholic solution of the fluoresceïn, crystallises in flat triclinic needles of golden-green lustre, containing 1 mol.  $C_2H_6O$ . The anhydrous compound melts at above  $310^\circ$ . It is very sparingly soluble in alcohol and ether, readily in alkalis, the solution appearing yellowish-red by transmitted, yellow by reflected light; in very dilute solution it appears carmine-red. Silk is dyed a fiery-red colour with slightly bluish tone; the colour being more intense than that given by a corresponding quantity of ordinary eosin. The alkali compounds can be obtained in small blue and green prisms of metallic lustre.

A. J. G.

**A New Terpene.** By C. LE NOBEL (*Chem. Centr.*, 1884, 184—185).—The author observed that the urine of a patient to whom copaiva balsam had been administered, gave a red coloration with hydrochloric acid. This reaction is due to a terpene,  $C_{20}H_{32}$ , which can be separated by Strauss's method. On boiling with soda solution, the separated oil is shaken up with much water, dilute hydrochloric acid added, and the milky solution filtered. A yellow oily substance remains on the filter; this is dissolved in 95 per cent. alcohol, and some time after filtering off, a white amorphous resin separates. The liquid is concentrated and yields an oil boiling at  $250$ — $260^\circ$ ; this is soluble in 95 per cent. alcohol, ether, amyl alcohol, and fatty oils, and sparingly in chloroform. The alcoholic solution becomes violet-blue with hydrogen chloride, and shows the characteristic absorption-bands described by Quincke. Besides this oil, the author found five resins, but failed to obtain a crystallisable acid. He considers this terpene to be the therapeutically active constituent of the balsam.

J. T.

**Monochlorobromo-camphor.** By P. CAZENEUVE (*Compt. rend.*, 100, 802—803).—By heating  $\alpha$ -monochloro-camphor with bromine in sealed tubes, chlorobromo-camphor,  $C_{10}H_{14}ClBrO$ , is obtained; it crystallises from alcohol in yellowish tufts. It melts at  $95$ — $96^\circ$ , is insoluble in water, sparingly soluble in cold, but readily soluble in hot alcohol and ether. Its specific rotatory power in chloroform solution is  $[\alpha]_D = +78$ . It cannot be distilled without decomposition and evolution of hydrogen bromide and chloride. From its crystalline form, its high point of fusion, and its sparing solubility in alcohol, it is preferably classed in the  $\alpha$ -series of camphor-derivatives.

V. H. V.

**Camphanic Acid.** By L. WARINGER (*Annalen*, 227, 1—12).—Bromocamphoric anhydride crystallises in the rhombic system;  $a : b : c = 0.8866 : 1 : 0.5766$ . Observed forms:  $\infty P$ , +  $\frac{P}{2}$ ,  $\infty P\bar{x}$ , —  $\frac{P}{2}$ , the last occurring but seldom.

*Camphanic acid* can be most conveniently prepared by heating a mixture of 10 grams of camphoric acid with 12 grams of bromine in sealed tubes at  $120^{\circ}$ . It crystallises in the monosymmetric system;  $a : b : c = 1.2723 : 1 : 1.522$ ;  $\beta = 66^{\circ} 34'$ ; observed faces  $\infty P$ ,  $0P$ ,  $\infty P\infty$ ,  $\frac{1}{3}P\infty$ , +  $P\infty$ . The barium salt,  $(C_9H_{13}O_4)_2Ba + 3\frac{1}{2}H_2O$ , forms large colourless crystals. When submitted to dry distillation, camphanic acid yields lauronolic acid, campholactone, and carbonic anhydride.

*Lauronolic acid*,  $C_8H_{13}\cdot COOH$ , is a colourless oil, sparingly soluble in cold water, readily soluble in ether and hot water. By heating with dilute hydrochloric acid, or even by long contact with the acid at the ordinary temperature, it is partially converted into the isomeric campholactone. *Calcium lauronolate*,  $(C_8H_{13}\cdot COO)_2Ca + 3H_2O$ , crystallises in colourless needles; the silver salt,  $C_{18}H_{13}\cdot COOAg$ , forms a white precipitate.

*Campholactone*,  $C_8H_{14}\langle \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ O \end{smallmatrix} \rangle$ , forms slender colourless needles, melts at  $50^{\circ}$ , and boils at  $230-235^{\circ}$ . It has a characteristic penetrating camphoraceous colour. Its behaviour when heated in aqueous solution resembles that of most of the other lactones. The corresponding *hydroxy-acid*,  $HO\cdot C_8H_{14}\cdot COOH$ , obtained by the action of hydrochloric acid on a solution of the barium salt prepared from the lactone, crystallises in colourless needles; it is very unstable, readily decomposing into water and the lactone.

A. J. G.

**Asarone.** By A. BUTLEROW and B. RIZZA (*Bull. Soc. Chim.*, **43**, 114).—The dried roots of *Asarum europæum* when distilled with steam yield 1.2 to 1.4 per cent. of asarone. Pure asarone melts at  $58-59^{\circ}$ , boils at  $296^{\circ}$ , has a sp. gr. of 1.165 at  $18^{\circ}$ , 1.0743 at  $60^{\circ}$ , and 1.0655 at  $90^{\circ}$  compared with water at the same temperatures; the coefficient of expansion of liquid asarone between the temperatures of  $60^{\circ}$  and  $90^{\circ}$  is therefore 0.00086. On heating asarone with an excess of hydriodic acid, methyl iodide is formed, together with a resinous substance soluble in alkaline solutions, from which it may be precipitated by acids; from the amount of methyl iodide obtained, it appears probable that the asarone molecule contains three methoxy-groups. By the oxidation of asarone with chromic acid in acetic acid solution, a neutral substance is obtained soluble in boiling water, from which it crystallises on cooling in long silky needles.

A. P.

**Jalapin.** By POLECK and SAMELSON (*Chem. Centr.*, 1884, 813).—The authors confirm the formula  $C_{34}H_{56}O_{16}$  ascribed to jalapin by Mayer. When treated with barium hydroxide, it is converted into barium jalapate according to the equation  $C_{34}H_{56}O_{16} + 2Ba(OH)_2 = 2C_{17}H_{28}O_9Ba + 2H_2O$ , so that jalapin must be looked upon as an anhydride of the bibasic jalapic acid. When treated with dilute hydrochloric acid, it yields grape-sugar, dextrose, and jalapinole. *Jalapinole* crystallises in needles melting at  $63^{\circ}$ , and has the properties of an aldehyde. Its formula is  $C_{16}H_{30}O_3 + \frac{1}{2}H_2O$ . With hydrogen potassium sulphite, it gives a crystalline compound,  $C_{16}H_{30}O_3\cdot HKSO_3$ . When acted on with potash, it yields bibasic

*jalapinic acid*,  $C_{16}H_{30}O_4$ , isobutyl alcohol, and a resin. Jalapinic acid crystallises in white needles which melt at  $64^\circ$ , and are easily soluble in alcohol, insoluble in water. When oxidised with potassium permanganate, jalapinic acid yields isobutyric and hydroxyisobutyric acids, and the author therefore considers it to be a condensation-product from 4 mols. of isobutaldehyde. When oxidised with permanganate, jalapinic acid yields isobutyric, hydroxyisobutyric, and oxalic acids, but with fuming nitric acid it gives isobutyric and ipomæic acids and carbonic anhydride. Ipomæic acid is isomeric but not identical with adipic acid.

L. T. T.

**Chlorophyll.** By R. SACHSSE (*Chem. Centr.*, 1884, 115—117).—Reviewing Schunck's research on this subject (*Abstr.*, 1884, 666), the author comes to the conclusion that the glucoside obtained by Schunck is probably identical with the "glucoside-like substance of chlorophyll" already described by himself (*Abstr.*, 1882, 67), to which he ascribes the formula  $C_{36}H_{80}O_{30}$ .

L. T. T.

**A New Colouring Matter from Chlorophyll.** By R. SACHSSE (*Chem. Centr.*, 1884, 113—115).—The author has previously (*Abstr.*, 1882, 65) described three derivatives of chlorophyll under the names of A-, B-, and C-phylocyanin. He now proposes as more suitable names  $\alpha$ -,  $\beta$ -, and  $\gamma$ -*phaeochlorophyll*, since they show the peculiar brownish-yellow colour of modified chlorophyll, and only become bluish-green in very strongly alkaline aqueous solutions. He is inclined to consider them as probably mixtures of the various colouring matters known as "modified chlorophyll," and thinks that the  $\gamma$ -compound may not be a distinct substance, but owe its easy solubility in alcohol to traces of fatty or waxy impurities.

$\beta$ -*Phaeochlorophyll*,  $C_{27}H_{33}N_3O_4$ , is a nearly black amorphous substance insoluble in water, soluble in benzene and boiling alcohol. Its aqueous solution turns green with potash or soda, reddish-brown with ammonia. When heated with baryta-water in closed tubes, or fused with soda, it loses carbonic anhydride, and yields a dark reddish-brown colouring matter,  $C_{26}H_{33}N_3O_2$ . This compound dissolves in alcohol to a dark-red solution which is changed to bright reddish-violet by the addition of a few drops of sulphuric acid. When mixed with soda and subjected to dry distillation, a dark red crystalline sublimate is formed and ammonia liberated. This sublimate when treated with hydrochloric acid and dilute alcohol yields a solution resembling the original violet solution. From this behaviour, the author thinks it may possibly bear a relation to the substance  $C_{26}H_{33}N_3O_2$  similar to that of pyrroline-red.

L. T. T.

**Colouring Matter of Leaves.** By M. ARNAUD (*Compt. rend.*, 100, 751—753).—The author has extracted from various species of spinach, peach, sycamore, &c., an orange-red colouring matter, which may be separated from chlorophyll by macerating the leaves in cold petroleum, chlorophyll being practically insoluble in this menstruum. The orange-red crystalline substance obtained after successive purifications, is identical with the erythrophyll of Bougarel and also with

carotene, obtained from various species of wild and cultivated carrot, the properties of which have been investigated by Zeise and Husemann.

V. H. V.

**$\alpha$ -Picoline,  $\gamma$ -Lutidine, and Pyridine.** By O. DE CONINCK (*Bull. Soc. Chim.*, **43**, 172—181).—Salts of aluminium, zinc, iron, mercury, manganese, barium, magnesium, bismuth, cobalt, and nickel, give very similar precipitates with either  $\alpha$ -picoline or  $\gamma$ -lutidine. Silver nitrate, however, gives a distinguishing reaction, as with  $\alpha$ -picoline no precipitate is formed, even after two days, whilst with  $\gamma$ -lutidine the solution at first shows a white turbidity, and after several hours a light brown precipitate is thrown down. Barium chloride, after remaining with  $\gamma$ -lutidine for several days or even weeks, gives a red coloration, whilst borax, under the same circumstances, yields an amethyst-violet colour, and potassium ferrocyanide a reddish-brown colour with the same base. Metallic sodium polymerises both  $\alpha$ -picoline and  $\gamma$ -lutidine, a magnificent dark blue colour being formed at the same time; this reaction takes place more rapidly with  $\alpha$ -picoline than with  $\gamma$ -lutidine.  $\beta$ -Lutidine is polymerised, and yields a red colour under the same circumstances; neither lutidine nor aniline yield similar reactions.  $\alpha$ -Picoline and  $\gamma$ -lutidine slowly absorb water from the air.

Synthetical and ordinary piperidine are, according to their reactions, absolutely identical. Pyridine, when treated with nickel or cobalt nitrate, does not yield a precipitate until warmed, whilst piperidine yields an immediate precipitate in the cold. Pyridine is not precipitated by magnesium chloride, but piperidine yields an immediate precipitate. The acetate and basic acetate of lead give very slight precipitates with pyridine, whilst with piperidine an immediate and heavy precipitate is formed. Piperidine gives an orange-yellow coloration with borax. Pyridine is polymerised by metallic sodium. Sodium alone seems to have the power of polymerising these alkaloids, as neither potassium, tin, zinc, iron, mercury, antimony, nor arsenic show this action, although tried in various states of division and at different temperatures. Piperidine platinochloride is not affected by boiling with water, but the platinochloride of pyridine is completely altered. Pyridine, like its homologues, is very hygroscopic, whilst piperidine is only slightly so. Piperidine absorbs carbonic anhydride, pyridine does not. Carbon bisulphide acts energetically on piperidine, but pyridine is acted on very slowly, small yellowish needles, of a compound not yet investigated, being formed. Nitrous acid acts rapidly on piperidine, the nitroso-derivative being formed; no such compound has been obtained from pyridine.

A. P.

**Homonicotic Acid.** By O. DE CONINCK (*Bull. Soc. Chim.*, **43**, 106—108).—When  $\beta$ -collidine is oxidised by means of potassium permanganate, a higher homologue of nicotic acid is obtained, to which the author gives the name of homonicotic acid  $C_5NH_3Me \cdot COOH$ ; when further oxidised this compound yields cinchomeric acid. Homonicotic acid is identical with the acid prepared by Hoogewerff and van Dorp by the oxidation of methylquinolinic acid, thus further establish-

ing the relation between the constitution of the pyridene and the quinoline series of alkaloids. A. P.

**Action of Phosgene Gas on Quinoline.** By E. OSTERMAYER (*Chem. Centr.*, 1884, 970).—The author has obtained a dichloroquinoline, apparently identical with that which La Coste obtained from metadichloraniline. L. T. T.

**A Homologue of Quinoline.** By C. BEYER (*J. pr. Chem.* [2], 31, 47—48).—By the action of nitrobenzene on the base  $\text{NPh} \cdot \text{CMe}_2$ , prepared from aniline and acetone, there was obtained, not as was expected, a methylindole, but a homologue of quinoline of the formula  $\text{C}_{11}\text{H}_{11}\text{N}$ . The *platinochloride*,  $(\text{C}_{11}\text{H}_{11}\text{N})_2, \text{H}_2\text{PtCl}_6$ , forms flesh-coloured needles and melts at  $227^\circ$ . The picrate melts at  $170^\circ$ . The free base forms a pale yellow oil of quinoline-like odour. H. B.

**Methochlorides of the Quinoline Series.** By E. OSTERMAYER (*Chem. Centr.*, 1884, 970).—These compounds are obtained by heating a quinoline-derivative with methyl alcohol and hydrochloric acid in closed tubes. *Quinoline methochloride*,  $\text{C}_9\text{NH}_7\text{MeCl} + \text{H}_2\text{O}$ , forms rhombic prisms melting at  $126^\circ$ . Quinoline methyl-picrate melts at  $164$ — $165^\circ$ . When an alcoholic solution of the methochloride is boiled with methyl iodide, it yields quinoline methiodide, melting at  $72^\circ$ . Bromine converts this into the bromine compound,



melting at  $123^\circ$ . When heated with zinc chloride at  $180^\circ$  the methochloride yields a base melting at  $112^\circ$ ; its formula is probably  $(\text{C}_9\text{NH}_7\text{Me})_2\text{O}$ , and it forms an aurochloride,  $(\text{C}_9\text{NH}_7\text{Me})_2\text{O}, \text{HAuCl}_4$ . *Tetrahydroquinoline methochloride*,  $\text{C}_9\text{NH}_{11}\text{MeCl} + \text{H}_2\text{O}$ , is crystalline and melts at  $244^\circ$ ; the picrate melts at  $125^\circ$ . *Hydroxyquinoline methochloride*,  $\text{C}_{10}\text{NH}_{10}\text{OCl} + \text{H}_2\text{O}$ , melts at  $210^\circ$ , and gives a deep green colour with ferric chloride. *Dimethamidoquinoline methochloride*,  $\text{C}_9\text{NH}_6(\text{NMe}_2)\text{MeCl} + \text{H}_2\text{O}$ , forms red needles melting at  $244^\circ$ , and when reduced with tin and hydrochloric acid yields *hydrodimethamidoquinoline methochloride*,  $\text{C}_9\text{NH}_{10}(\text{NMe}_2)\text{MeCl} + 2\text{H}_2\text{O}$ , which melts at  $220^\circ$ . *Diquinoline methochloride*,  $\text{C}_{18}\text{N}_2\text{H}_{12}\text{Me}_2\text{Cl}_2 + 6\text{H}_2\text{O}$ , forms colourless needles melting at  $260^\circ$ . L. T. T.

**Iodine Chloride and its Action on Organic Compounds (especially on Quinolines and Alkaloids).** By E. OSTERMAYER (*Chem. Centr.*, 1884, 937—938).—The iodine chloride having, according to Schützenberger, the formula  $\text{ICl}, \text{HCl}$ , was prepared by slowly adding 500 grams sodium nitrite to a mixture of 500 grams potassium iodide dissolved in water and 2 litres concentrated hydrochloric acid. This solution, freed from nitrous acid by boiling, is stable towards light. It is a very good reagent for the preparation of iodated organic compounds. Aniline, for instance, at once yields *pariodaniline* when treated with this solution.  $\beta$ -Naphthol gave a new  $\beta$ -*moniodonaphthol*, melting at  $88^\circ$ .

Its action with quinoline and alkaloid bases is, however, quite different. Quinoline yields *chloridoquinoline hydrochloride*,



forming dark red needles melting at  $118^\circ$ . Water liberates the base  $\text{C}_9\text{NH}_7\text{I}$ , which crystallises in yellow needles and melts at  $158^\circ$ . Picric acid with the base simply yields quinoline picrate, but chromic acid forms a salt of the composition  $\text{C}_9\text{NH}_7\text{I}\cdot\text{H}_2\text{CrO}_4$ , melting at  $160^\circ$ . With chlorine, the hydrochloride yields  $\text{C}_9\text{NH}_7\text{I}\cdot\text{Cl}_3\cdot\text{HCl}$ , melting at  $180^\circ$ . Hydroxyquinoline gives with this reagent *diiodohydroxyquinoline hydrochloride*,  $\text{C}_9\text{NH}_4(\text{OH})\text{I}_2\cdot\text{HCl}$ , which melts at  $100^\circ$ , and is converted by water into *diiodohydroxyquinoline*, melting at  $205^\circ$ . Quinoline methochloride yields *chloridoquinoline methochloride*, crystallising in yellow scales melting at  $112^\circ$ . The methiodides lose all their iodine and are converted into the methochlorides. Diquinoline takes up 2 mols. of the iodine chloride.

Cinchonic acid yields yellow needles of the compound



melting at  $190^\circ$ ; pyridine gives *chloridopyridine hydrochloride*,  $\text{C}_5\text{NH}_5\text{I}\cdot\text{HCl}$ , melting at  $178^\circ$ . Cinchonine gives a compound melting at  $215^\circ$ ; quinine a compound,  $\text{C}_{20}\text{N}_2\text{H}_{24}\text{O}_2\text{I}_3\text{Cl}\cdot 2\text{HCl}$ .

L. T. T.

**Iodated Azo-colouring Matters.** By E. OESTERMAYER (*Chem. Centr.*, 1884, 970—971).—Sodium naphtholsulphonate yields with iodine chloride (see preceding Abstract) an *iodonaphtholsulphonic acid*; naphthionic acid, an *iodonaphthylaminesulphonic acid*. The first of these, when treated with diazobenzene chloride, yields a scarlet powder, which dyes silk and wool orange. Its formula is probably  $\text{PhN}_2\cdot\text{C}_{10}\text{H}_4\text{I}(\text{OH})\cdot\text{SO}_3\text{K} + \text{H}_2\text{O}$ . The same acid yields with diazoxylene chloride, scarlet scales of ammonium xyleneazoiido- $\beta$ -naphtholsulphonate,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_4\text{I}(\text{OH})\cdot\text{SO}_3\text{NH}_4$ . *Iodocroceïn-scarlet*, from the same acid and diazobenzenesulphonic acid, very closely resembles croceïn. Iodonaphthionic acid gives similar colouring matters, but they are of a browner shade and decompose rapidly. In general, the introduction of iodine hardly affects the colour of the compound.

L. T. T.

**Colouring Matters from Lepidine.** By S. HOOGWERFF and W. A. VAN DOERP (*Rec. Trav. Chim.*, 2, 317—326). The authors find that when a mixture of equal molecular proportions of an alkyl iodide of quinoline with a similar compound of lepidine is treated with potash, a new compound is formed according to the equation  $\text{C}_9\text{NH}_7\cdot\text{XI} + \text{C}_{10}\text{NH}_9\cdot\text{YI} = \text{C}_{15}\text{N}_2\text{H}_{13}\cdot\text{XXI} + \text{HI} + \text{H}_2$ , where X and Y represent any monad alcohol radicle. They at present designate the radicle  $\text{C}_{10}\text{N}_2\text{H}_{15}$  *cyanine*, as they believe it to be similar in composition to the compound of that name obtained by G. Williams (*Dingl. polyt. J.*, 159, 330 and 399) by the action of amyl iodide and potash on commercial quinoline.

*Dimethyleyanine iodide*,  $\text{C}_{19}\text{N}_2\text{Me}_2\text{H}_{13}\text{I}$ , is obtained when a mixture of quinoline and lepidine methiodides is employed. It dissolves slightly in water, giving a bluish-red solution, and in alcohol to a solution



which is blue by reflected, violet by transmitted light. Acids dissolve it to a yellow solution, and hot dilute ammonia dissolves the salt, but deposits it again on cooling. It melts at  $291^{\circ}$ , and is capable of forming double compounds with many metallic salts. When its alcoholic solution is digested with silver chloride, the corresponding chloride is formed. This forms a green mass with a metallic lustre, and yields a yellow platinumochloride.

*Diethylcyanine iodide* forms green glistening prisms which melt at  $271-273^{\circ}$ . It resembles the dimethyl-compound in character.

The quantity of cyanine-derivative obtained in these reactions is about half that required by theory, other colouring matters (which the authors have not yet succeeded in isolating) being formed at the same time, so that the reaction may possibly be more complicated than that given above. The authors have repeated Williams' experiments with *pure* quinoline, and could obtain no cyanine. Its formation was undoubtedly due to the presence of lepidine in the commercial product employed by him. The authors have obtained an analogous compound with a mixture of lepidine and Skraup's paratoluquinoline.

L. T. T.

**Carnine.** By C. KRUCKENBERG and H. WAGNER (*Chem. Centr.*, 1884, 107).—The authors obtain carnine by boiling with water the precipitate thrown down from meat extract by lead acetate. On evaporating to a small bulk, the carnine crystallises out after some days. A table given with the original memoir gives the reactions of carnine, xanthine, hypoxanthine, paraxanthine, guanine, and a xanthine-like substance obtained by the authors from alligator muscle, with silver nitrate, lead acetate, copper acetate, mercuric chloride, mercuric nitrate, picric acid, and aqueous soda. Carnine is not widely diffused. The authors found it in some fresh-water fish, frog's flesh, but not in alligator muscle or in *Æthaliium septicum*.

J. T.

**Caffeine Methylhydroxide.** By E. SCHILLING (*Chem. Centr.*, 1884, 811).—The union of the methyl-group to caffeine in its methiodide, methochloride, and methylhydroxide is a very loose one, these compounds being decomposed at about  $200^{\circ}$ , the products of decomposition of the methylhydroxide being sarcosine, methylamine, carbonic anhydride, and formic acid. With caffeine methylhydroxide, bromine yields an additive product which is decomposed by water into allocaffeine, cholestrophane, methylamine, and hydrobromic acid. When oxidised with chromic acid, caffeine methylhydroxide yields cholestrophane, methylamine, and formic and carbonic acids; with hydrochloric acid and potassium chlorate, it yields dimethylalloxan, allocaffeine, amalinic acid, cholestrophane, and methylamine; with nitric acid, cholestrophane, methylamine, and carbonic anhydride. When acted on by barium hydroxide, caffeine methylhydroxide yields sarcosine, methylamine, formic acid, and carbonic anhydride.

Allocaffeine is probably a methylated apocaffeine, and the acid formed from it by the action of water, a methylcaffuric acid. Ammonia is found amongst the decomposition products of caffeine, but amongst those of caffeine methylhydroxide only methylamine is found, and never ammonia. The author considers that the present

information is not sufficient to decide between the merits of the formulæ for caffeine methylhydroxide proposed respectively by Medicus and E. Fischer.

L. T. T.

**Dicinchonicine.** By O. HESSE (*Annalen*, **227**, 153—161).—Dicinchonicine,  $C_{38}H_{44}N_4O_2$  (termed dicinchonine by the author), occurs principally in *Cinchona rosulenta* and *C. succiruba*; in the first, it occurs to the extent of about 0·2—0·3 per cent., and is accompanied by cinchonidine, homocinchonidine, and cinchonine, together with traces of quinamine and quinidamine. The method of separation from the accompanying alkaloids is described. Dicinchonicine forms a yellowish powder readily soluble in ether, acetone, alcohol, chloroform, and benzene, sparingly in water and light petroleum, insoluble in soda. Its alcoholic solution has a strongly alkaline reaction, a bitter taste, does not give any coloration with chlorine or potassium hypochlorite and ammonia, and has the rotatory power  $[\alpha]_D = +65\cdot6^\circ$ . The hydrochloride,  $C_{38}H_{44}N_4O_2 \cdot 2HCl$ , crystallises in colourless prisms; the platinochloride,  $C_{38}H_{44}N_4O_2 \cdot 2H_2PtCl_6 + 4H_2O$ , is obtained as an amorphous yellow precipitate; the hydriodide forms compact colourless crystals, the oxalate crystallises in large colourless prisms.

A. J. G.

**Strychnine.** By H. BECKURTS (*Chem. Centr.*, 1884, 812).—*Strychnine ferrocyanide*,  $(C_{21}H_{22}N_2O_2)_4 \cdot H_4Fe(CN)_6 + 4H_2O$ , crystallises in yellowish needles or prisms. When exposed to the air and light, it absorbs oxygen, and is converted into strychnine ferricyanide, water, and free strychnine. Pure strychnine crystallises in anhydrous tetragonal prisms melting with decomposition at  $285^\circ$  (uncorr.). The author has prepared and examined mono- and di-bromostrychnine and many of their salts, and also tribromostrychnine. The latter compound he considers to be a mixed substitution and additive product, as it is always formed during the preparation of monobromostrychnine, but is immediately converted into the latter substance when brought into contact, by stirring, with fresh strychnine. He believes that no more highly brominated compounds of strychnine exist than the tribromo-derivative.

L. T. T.

**Hydrastine.** By F. B. POWER (*Chem. Centr.*, 1884, 938—939).—When carefully purified, this alkaloid yields colourless shining crystals which melt at  $132^\circ$  and are insoluble in water, soluble in acids, alcohol, benzene, &c. The rotatory power in a chloroform solution is  $\alpha[\alpha]_D = -170^\circ$ . When heated with strong sulphuric acid, hydrastine turns red, and with ammonium molybdate and strong sulphuric acid green. Its formula is  $C_{22}H_{23}NO_6$ . When acted on by nascent hydrogen, hydrastine appears to yield *hydrohydrastine*,  $C_{22}H_{27}NO_6$ . When fused with potash, it gives formic and protocatechuic acids. With ethyl iodide, it forms *ethylhydrastine*,  $C_{22}H_{22}EtNO_6$ , from which reaction the author considers hydrastine to be an imide-base. The ethyl derivative melts at  $183^\circ$ .

Even when working up some thousands of pounds of *Hydrastis canadensis*, the author was unable to obtain the third alkaloid xanthopucine said to be present therein.

L. T. T.

**Behaviour of Lupinidine with Ethyl Iodide.** By G. BAUMERT (*Annalen*, **227**, 207—220).—When lupinidine is heated with ethyl iodide at 100°, a complete reaction can never be obtained, both lupinidine and ethyl iodide being found in the product. The substances formed are lupinine ethiodide, and what would seem to be a basic lupinidine ethiodide,  $C_{21}H_{40}N_2O_2 \cdot 2EtI$ .  
A. J. G.

**Fagine.** By J. HABERMANN (*Chem. Centr.*, 1884, 789—790).—As the statements given regarding this substance, said to be contained in beech-nuts, are so very contradictory, the author has attempted to isolate it. He was most successful with an extract made by digesting bruised beech-nuts with water at 0—8°. After very careful purification, he obtained a very small quantity of a substance which had the properties of an alkaloid. When acidified with a few drops of hydrochloric acid and evaporated, he obtained a few crystals, which appeared under the microscope to be 8-rayed stars, four of the rays being much more fully developed than the others. The substance was only very small in quantity, and still far from pure. The author, however, believes that the existence of fagine as a true alkaloid cannot be doubted.  
L. T. T.

**Leucomaines.** By A. GAUTIER (*Bull. Soc. Chim.*, **43**, 158—162).—Bacterial ferments acting on albuminoids invariably produce certain poisonous alkaloids, which appear to be identical with those hitherto known as ptomaines; as, however, they are constant and necessary principles in the normal excretions of living organisms, and have been detected in the saliva, urine, muscular juices, sweat, and also in numerous glands, it is proposed to designate them leucomaines (*λευκωμα* = white of an egg). They are mostly poisonous, crystalline, and give crystalline platinochlorides. A *hydrocollidine*,  $C_8H_{13}N$ , obtained from the putrefaction of albuminoids, is oxidised by the air, boils at 200—210°, reduces salts of gold, and gives a platinochloride easily altered by heat.  
A. P.

**Ptomaines in Boiled Meat.** By H. MAAS, BUCHMANN, and WASMUND (*Chem. Centr.*, 1884, 975).—The authors have examined raw and boiled meat in regard to the formation of poisonous alkaloids. They find that during putrefaction poisonous alkaloids are formed quite as rapidly, if not more rapidly, in boiled than in raw meat. The quantity formed increases for some time, but with continued putrefaction again decreases. They also find that the cases of poisoning from fish are due to poisonous alkaloids which have been formed therein.  
L. T. T.

**Animal Colouring Matters.** By MIHAILOFF (*Bull. Soc. Chim.*, **43**, 123).—On treating glycocholic acid in the presence of acetic acid with an excess of concentrated sulphuric acid, an orange-yellow liquid, having a deep green fluorescence, is obtained; adding a saturated solution of ammonium sulphate to this, it yields a precipitate of a colouring matter, which by its reaction appears to be biliverdin. The solution contains urobilin. By acting in the same way on albu-

minoïds, urobilin is obtained, but no biliverdin; it appears, therefore, that the hydrogen sulphide formed by the action of the sulphuric acid on albuminoïds prevents the transformation of urobilin into biliverdin. By adding the theoretical quantity of ammonium hydrogen sulphide to a slightly acid solution of biliverdin, it is transformed into urobilin. A. P.

**The Mucin-group.** By O. HAMMARSTEN (*Chem. Centr.*, 1884, 814).—The author points out that there can now be no doubt that mucins from various sources are of varying composition. He considers the three most typical properties of mucins to be their characteristic toughness and elasticity, the formation of a reducing substance when treated with dilute acids, and their precipitation by acetic acid. By careful treatment with potash at the ordinary temperature, it has also been possible from all mucins hitherto examined to obtain a carbohydrate, which is apparently identical with Landwehr's "animal caoutchouc." This carbohydrate yields the reducing substance mentioned above when heated with dilute acids. L. T. T.

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## Physiological Chemistry.

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**Respiration in Compressed Air.** By N. SUCHORSKY (*Chem. Centr.*, 1884, 673).—The following conclusions are drawn:—The absolute amount of oxygen inspired and of carbonic anhydride expired is diminished in compressed air. The reduction of the amount of carbonic anhydride is influenced directly by the reduced volume of air breathed. The percentage of carbonic anhydride in the compressed air is almost the same as in air at ordinary pressures. The amount of oxygen consumed diminishes by a somewhat less extent than the amount of carbonic anhydride expired. A relatively larger amount of oxygen is consumed in compressed air than in ordinary air. All these effects of compressed air are the more intensified, the more the difficulty of breathing is increased by change in the conditions, or by pathological changes in the respiratory organs. The deviations from these rules depend usually on simultaneous changes in the number and depth of the respirations. The rhythm of the respiration remains unchanged. In all cases of mechanical hindrance (bronchitis), restriction of excursion of the organs (pleuritis), or reduction of surface (pneumonia), the change of rhythm consists in a gradual disappearance of the pause after expiration, and the times of inspiration and expiration become equal. Compressed air acts on the circulation in a two-fold manner; on the one side it compresses all the capillaries of the outer surface and of the respiratory organs, causing a more complete emptying of the veins, and on the other side changes the distribution of blood in the system, causing an accumulation in

the abdominal organs. The therapeutic action of compressed air may be referred exclusively to its mechanical action on the organisation, and to the increase of partial oxygen pressure. The latter produces no perceptible effect on the oxidation process in the body; on the contrary, in pathological cases where respiration is impeded, it tends to reduce the absolute amount of oxygen taken up and the carbonic anhydride expelled, as the organism obtains the necessary amount of air with less difficulty, and so the muscular work of the respiratory organs is economised. Consequently, the therapeutical application of compressed air cannot be considered as facilitating oxidation and support of the body in sick cases, but as a saving of effort. Nevertheless it would be erroneous to conclude that compressed air might in these cases be replaced by air rich in oxygen, since the compressed air exerts a series of favourable influences on the sick organisation, and especially on the respiratory organs. The pressures employed varied between 1045 and 1143 mm. of mercury.

J. T.

### Alimentary Value of the Different Parts of the Wheat Grain.

By A. GIRARD (*Ann. Chim. Phys.* [6], 3, 289—355).—Although the envelope of the wheat grain (14·36 per cent. the weight of the whole) is rich in nitrogenous substances (containing 18·75 per cent.), yet these substances are shown by direct experiments of the author's to be incapable of assimilation by the human alimentary system, which practically leaves the envelope unaltered. Further, amongst these nitrogenous substances is included the ferment discovered by Mège-Mouriès, and named by him *cerealin* (*Compt. rend.*, 50, 407, &c.). This substance acts on starch in a manner nearly like that of diastase, and during the fermentation in the process of bread-making, it modifies the gluten of the flour, removing its plasticity, and imparting to it the brown colour which in bread prepared from "entire flour" is commonly but erroneously attributed to the bran diffused through the mass. In these and other ways it therefore deteriorates the quality of bread. There are assimilable mineral substances contained in the bran to the extent of 0·4 per cent. of the whole grain, while the purely farinaceous internal parts contain 0·6 per cent. of such mineral substances; but considering the variety of materials now used for food, the gain in this respect must be regarded as unimportant, and as not compensating for the inconveniences attending the presence of the envelope in the flour. Again, although the embryo or germ contained in the wheat grain is rich in nitrogenous substances, and these probably assimilable, it also should be eliminated from the flour, because it contains not only *cerealin*, but also a highly oxidisable oil, capable of imparting the odour of rancid grease to the whole mass. Only the inner farinaceous portion of the grain should therefore be used for human alimentation, and it should be the aim of the miller to completely eliminate from his flour all the other parts. These, however, need not be lost, for as animals have a larger range of digestive power than man, it is possible that the materials we may properly reject from our bread, may be received again when transformed into flesh.

R. R.

**Use of Milks Preserved by High Temperatures (100° C.) for Children's Food.** By A. BAGINSKY (*Chem. Centr.*, 1884, 43).—In milks preserved by either the Romanshorn or the Scherff method, the solubility of the casein in water is increased. The amount of albumin present appears to be much diminished. Rennet acts on the preserved milks much less effectively than on fresh cow's milk, having little or no action at 15°, and even at 53° it is necessary to use at least twice the quantity to produce an effect equal to that produced on fresh milk. Both varieties of preserved milk, on being artificially digested with rennet and hydrochloric acid, yield products quite similar to those obtained from fresh cow's milk under the same circumstances. A child may be successfully fed on milk preserved by Scherff's method, no more of the preserved milk being required than would be needed of fresh cow's milk. A. P.

**Digestion in the Horse.** By ELLENBERGER and HOFMEISTER (*Bied. Centr.*, 1885, 100—101).—In this paper, which is a continuation of a previous article (this vol., p. 178), the experiments made to ascertain the peculiarities of the extract of the digestive organs of the horse are detailed.

The results obtained are as follows:—

	Aqueous extract of the					
	Duodenum.	Jejunum.	Ileum.	Cæcum.	Colon.	Rectum.
Colour .....	opaque white	opalescent	opalescent	opaque white	opalescent	opalescent
Consistence.....	thick ropy	thin	thin	thin	thin	thin
Reaction .....	acid	acid	neutral	neutral	neutral	neutral
Mucin .....	much	little	little	much	much	little
Pepton .....	trace	<i>nil</i>	<i>nil</i>	<i>nil</i>	<i>nil</i>	<i>nil</i>
Hemialbumin.....	much	<i>nil</i>	<i>nil</i>	trace	trace	<i>nil</i>
Xanthoprotein reaction.	strong	feeble	feeble	strong	strong	strong
Chlorides.....	trace	<i>nil</i>	<i>nil</i>	trace	trace	trace
Sulphates.....	little	?	?	light	little	little
Phosphates.....	do.	trace	trace	do.	do.	<i>nil</i>

Sugar and odour absent.

The experiments were made by means of starch paste, cellulose, and egg albumin; the action on starch showed the presence of a diastatic ferment, which was destroyed by heat and by putrefaction; freezing only checked its action, without destroying it. Albumin was undissolved except by the extract from the beginning of the duodenum, and then only in presence of acid. The emulsive action on fat is possessed by the juices, but they are not capable of decomposing it. On cellulose the juices have no special action; a fuller account is reserved for a future publication. E. W. P.

**Carbohydrates in Human Liver.** By KRATSCHMER (*Chem. Centr.*, 1884, 184).—The *post mortem* formation of sugar goes on in the liver from a healthy or diseased subject, up to a certain extent, and quite independently of the amount of glycogen present at the time. Since the glycogen remains intact for a time, the sugar must come from

other sources. The degree of fulness of the alimentary canal does not in general influence the result. Cases occur in which, with considerable amounts of sugar, no trace of glycogen occurs, whilst in other cases, in the liver of the lower animals as well as of the human subject, the glycogen has not been attacked. In pathological cases, both sugar and glycogen may completely disappear from the liver. The livers of both men and animals afford a substance containing both nitrogen and sulphur, which has not yet been described. When a liver free from sugar and glycogen, is de-albuminised by treatment with hydrochloric acid and potassium mercury iodide, and the clear filtrate is mixed with 5 to 6 times its amount of 90 per cent. alcohol, a small snow-white flocculent precipitate is obtained, in appearance exactly like glycogen. This shrinks to gum-like flocks on the filter, is largely dissolved by water, and can be reprecipitated by alcohol. Neither saliva nor mineral acids convert it into sugar; it contains nitrogen and sulphur, is not precipitated by phosphotungstic acid, but is precipitated by potassium mercury iodide, and is distinguished by this and other reactions from albumin, peptone, mucin, and gluten. It also occurs in livers which contain sugar and glycogen. J. T.

**Uric Acid from the Green Glands of *Astacus Fluviatilis*.**

By A. B. GRIFFITHS (*Chem. News*, 51, 121—122).—The secretion of the green gland of the fresh water crayfish (*Astacus fluviatilis*) is acid to litmus-paper, and contains notable quantities of uric acid and traces of guanine. D. A. L.

**Acetonuria.** By R. v. JACKSCH (*Chem. Centr.*, 1884, 674—675, see Abstr., 1883, 1161).—The most sensitive test for acetone is Lieben's iodoform reaction, which shows 0.01 mgrm. of acetone at once, and even 0.001 to 0.0001 mgrm. after a time. Next to Lieben's comes Gunning's modification of it, where ammonia is substituted for fixed alkali; then follows Reynold's test which depends on the solubility of freshly precipitated mercuric oxide in a liquid containing acetone. The test of Legal, Le Nobel, and Penzoldt are less sensitive. Lieben's test also gives a reaction with alcohol, but it is less sensitive with this than with acetone. The author prefers Lieben's test, which is applied to the distillate from the urine. He holds it highly probable that acetone occurs in urine as such. The author has found that the acetone reaction is only obtained with the blood of fever patients. He also found in the exhalations of a fever patient, a substance which gave the reaction. The contents of the stomach contain acetone, but the origin of it has not yet been made out. The fæces of healthy subjects contain a substance which gives iodoform; in certain sick cases, especially those in which much acetone is found in the urine, the fæcal distillate gives iodoform, even with ammonia and tincture of iodine. The detection of acetone in fæces and the contents of the stomach is, however, more difficult than in the blood. J. T.

**Turbidity of Albuminous Urine on Heating.** By B. J. STOKVIS (*Chem. Centr.*, 1884, 42).—The precipitate obtained when many albuminous urines are heated is due to the decomposition of the



soluble dihydrogen dicalcium phosphate occurring in urine into monocalcium phosphate which remains in solution, and tricalcium phosphate which is precipitated:  $2\text{Ca}_2(\text{HPO}_4)_2 = \text{Ca}_3(\text{PO}_4)_2 + \text{Ca}(\text{H}_2\text{PO}_4)_2$ . On cooling, the reverse action takes place, and the precipitate redissolves. Calcium sulphate and oxalate are often present in small quantities in the precipitate, whilst magnesium compounds are usually absent.

A. P.

### Composition of the Precipitate obtained on Heating Urine.

By W. G. SMITH (*Chem. Centr.*, 1884, 42).—The author arrives at the same conclusions as Stokvis concerning the precipitation of tricalcium phosphate (preceding Abstract). An aqueous solution of the monocalcium phosphate was just neutralised with ammonia: on warming, a precipitate was formed; this was partly redissolved on cooling. Mixtures of dihydrogen potassium phosphate and calcium chloride did not show this reaction, but on using the sodium instead of the potassium salt, the same results were obtained as with the urine itself.

A. P.

**Physiological Action of Nickel Salts.** By F. GURKENS (*Chem. Centr.*, 1884, 43).—Nickel salts, like those of mercury and arsenic, when absorbed into the system, set up inflammation in the glands of the intestinal tract. Nickel acetate acts with much greater energy when injected subcutaneously, than when taken through the stomach, as in the latter case, absorption of the poison is largely prevented by the formation of insoluble nickel compounds.

Nickel salts, especially the chloride, show antiseptic properties, preventing the decay of animal matter, although the growth of mould on vegetables is but little affected.

A. P.

**Physiological Action of Nitroglycerol.** By M. HAY (*Chem. Centr.*, 1884, 108).—The poisonous action of nitroglycerol cannot be explained by the action of its constituents. The symptoms are similar to those produced by amyl and potassium nitrites. The author found that of the three  $\text{NO}_2$  groups present in nitroglycerol, only one is removed by the action of alkalis as nitrate, the other two combining with the alkali as nitrite, whilst the oxygen set free oxidises the regenerated glycerol. An alcoholic nitroglycerol solution reacts rapidly in this sense with an alcoholic sodium hydroxide solution, with development of much heat. The formation of nitrite, however, occurs even on digesting at  $40^\circ$  an aqueous solution of nitroglycerol (1:800), with a little sodium hydroxide (0.2 per cent.); the reaction being complete in about ten minutes. Blood at the temperature of the body acts similarly upon nitroglycerol; the blood becomes chocolate coloured, as is the case when it is exposed to the action of amyl or potassium nitrite. Spectroscopic observation reveals the metahæmoglobin band. Reducing agents reproduce the red colour of hæmoglobin, as in the case of the nitrites above mentioned. Hence nitroglycerol acts by its conversion into nitrite.

J. T.

**Physiological Action of  $\beta$ -Collidine Hexahydride.** By BOCHEFONTAINE and O. DE CONINCK (*Compt. rend.*, 100, 806—808).—

$\beta$ -Collidine hexahydride is obtained by the direct addition of six atoms of hydrogen to  $\beta$ -collidine derived from cinchonine, in accordance with the equation  $C_8H_{11}N + 8H_2 = C_8H_{17}N$ . When hypodermically injected into the frog, it affects the cerebro-spinal and vasomotor systems and finally the pulsations of the heart, but with mammalia it produces death by general debilitation and stoppage of the respiration. In its general behaviour, it resembles curari, but more closely cicutine (Abstr., 1884, 1047), its isomeride obtained from  $\beta$ -lutidine.

V. H. V.

**Physiological Action of Cinchonamine.** By G. SÉE and BOCHEFONTAINE (*Compt. rend.*, 100, 644—646).—There is no true antagonism between cinchonamine and digitaline, but if equivalent and fatal doses of the two are injected simultaneously, the action of the heart of a frog continues to be regular, but the animal eventually dies, owing to the action of the cinchonamine on the nervous centres. The injection of cinchonamine sulphate causes a very marked increase in the secretion of saliva, due to a direct action of the alkaloïd on the salivary gland. At the same time, the secretion of urine is not affected, whilst the secretion of bile seems to be augmented, but the effect on the pancreatic juice was not definitely ascertained. Convulsions are produced by the introduction of cinchonamine into the stomach, as well as by injecting it into the veins, and these convulsions are accompanied by a *reduction* of the arterial pressure, whereas the convulsions produced by strychnine and substances of the same kind are accompanied by an increase of arterial pressure. This reduction of arterial pressure has, however, already been observed by one of the authors in the case of the convulsions produced by the injection of cinchonine, cinchonidine, and even quinine. The three last alkaloïds produce vomiting when introduced into the stomach of the dog, but the introduction of cinchonamine in this way produces the same effect as when it is injected into the veins and does not cause vomiting.

C. H. B.

**Physiological Action of Ptomaïnes.** B. v. ANREP (*Chem. Centr.*, 1884, 107, comp. Abstr., 1883, 1157—1159).—The alkaloïds prepared from musty rye-meal or from mixtures of the meal with pepsin or ergot, show toxic properties. These substances exert a poisonous action on frogs, but not on warm-blooded animals; the symptoms being the same, whether extracts from pure meal, meal with pepsin, or meal with ergot, were employed. The strength of the poison extracted increased with the degree of putrefaction of the meal. The extract from meal with addition of 5 per cent. ergot, or with pepsin, was always more poisonous than the extract from pure meal. There appears to be no difference in the intensity of action of the extract from meal and ergot, and the extract from meal and pepsin. The author describes experiments on frogs; the negative results obtained with warm-blooded animals are not held to be conclusive. J. T.

**Action of Potassium Nitrite on Blood.** By A. HÉNOQUE (*Chem. Centr.*, 1884, 107).—The blood of an animal which has been poisoned

by sodium nitrite has a brownish colour, owing to the partial conversion of hæmoglobin into metahæmoglobin. J. T.

**Action and Metamorphosis of some Substances in the Animal Organism in Relation to Diabetes.** By K. ALBERTONI (*Chem. Centr.*, 1884, 142, from *Italia Med.*, 1883).—Acetone is not injurious, and even in large doses produces only intoxication. When given to healthy persons in larger doses than 3 c.c. it is passed unchanged. When alcohol, glucose, or butyric acid was given to dogs or rabbits, neither acetone nor acetoacetic acid could be detected in their urine. Isopropyl alcohol is partly converted into acetone, partly passed unchanged. Ethyl acetoacetate or acetoacetic acid produce nothing like *coma diabeticum*, but sometimes cause the urine to become very albuminous. Levulinic acid causes prostration and rapid death: its formation may possibly be the cause of the sudden death sometimes occurring from diabetes. L. T. T.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Formation of Free Hydrochloric Acid in Plants.** By W. DETMER (*Ann. Agronom.*, **11**, 88—89; from *Bot. Zeit.*, 1884, 791—797).—By using methylaniline violet as an indicator, it can be shown that citric acid and other organic acids possess the power of partially decomposing chlorides in solution at the ordinary temperature, and liberating hydrochloric acid. A solution of 0.02 gram citric acid in 15 c.c. water scarcely changes the colour of this indicator; but if 0.7 gram of sodium or potassium chloride be added some hours before testing, the colour of the methylaniline violet is changed to blue—the same change being produced by very dilute hydrochloric acid. Chlorides do not affect methylaniline violet. A trace of chloride promotes the action of diastase on starch; according to the author this is because the organic acids of the malt infusion liberate a little hydrochloric acid. Too much hydrochloric acid, however, retards the action.  
J. M. H. M.

**Micro-organisms in the Soil.** By E. WOLLNY (*Bied. Centr.*, 1885, 73—82).—In this communication, which is a continuation of a former paper (this vol., p. 426), the author details the changes which occur in the physical condition of the soil under the influence of the various processes of cultivation, but the matter is more of agricultural than of chemical interest.  
E. W. P.

**Formation of Starch in Vine Leaves.** By G. CARBONI (*Ann. Agronom.*, **11**, 85—86; from *Rivista de Vitisoltura ed Enologia Italiana*, **9**, 13).—The author has applied to this study Sachs' method of blanching the leaves by the successive action of potassium hydroxide

and absolute alcohol, and subsequently immersing them in a saturated solution of tincture of iodine : the amount of starch present is judged by the depth of coloration attained. None of the leaves examined contained starch before April 28th, but by the 12th of May the formation of starch was general, and it continued until November. The starch formed in the leaves during sunshine disappears during the night. At 4 o'clock on the morning of June 25th, half of a leaf was removed, the other half being left attached to the midrib. The half removed contained no starch, but two hours afterwards the half which remained was found fully charged with starch, which however disappeared by the next morning. The youngest leaves do not form starch, and the older leaves cease to form it after a certain time. Hence the justification of pinching out the young shoots formed too late to be of any use to the plants, and of removing the old leaves below the grape clusters.

J. M. H. M.

**Formation and Physiological Significance of Gum.** By A. B. FRANK (*Ann. Agronom.*, **11**, 86—87; from *Ber. Deutsch. bot. Gesells.*, **11**, 1884).—As to the origin of gum, the author agrees with Prillieux that it is a product of the transformation of the materials contained in living wood cells, and that it finds its way through the tissues by means of the punctures existing in the walls of the vessels and fibres. He considers its physiological function to be that of providing a watertight and airtight closure to surface wounds caused by insects, frosts, accident, fall of the leaves, &c. The gum formed in woody fibre is insoluble in water and does not swell when moistened.

J. M. H. M.

**Chemical Composition of *Artemisia Gallica*.** By E. HECKEL and F. SCHLAGDENHAUFFEN (*Compt. rend.*, **100**, 804—806).—The therapeutic value of *Artemisia gallica*, a plant common in France, has been completely neglected, for the santonin of commerce is for the most part obtained from species of *Artemisia* indigenous to Russia and Turkestan. In this note, it is shown that the French species contains about 1 per cent. of an essential oil, together with a crystalline substance, probably camphor; from the flower heads, wax, a yellow colouring matter, and chlorophyll can be extracted by petroleum; a considerable proportion of santonin, together with a resinous substance, apparently an isomeride of santonin, by chloroform, and glucose, tannin, a colouring matter and a substance giving all the characteristic reactions of an alkaloid by alcohol. The presence of the last substance is worthy of interest, inasmuch as hitherto no organic base has been found in plants containing santonin.

V. H. V.

**Composition of *Furze* (*Ulex Europæus*).** By TROSCHKE (*Bied. Centr.*, 1885, 115—116).—The two samples of this plant, which is largely used for fodder, were cut in October, and were received (1) crushed, the other (2) in a natural state. The analyses are as follows :—

	1.	2.
Water .....	54.00 p. c.	60.7 p. c.
In the dry substance—		
Ash .....	5.19 „	3.89 „
Albuminoids .....	9.84 „	11.25 „
Fat .....	2.09 „	3.00 „
Fibre.....	47.16 „	45.66 „
Cellulose, &c. ....	35.72 „	36.20 „
Nitrogen .....	1.57 „	1.80 „
N. as albumin .....	1.38 „	1.62 „
N. as amides .....	0.19 „	0.18 „
N. soluble after diges- tion .....	0.74 „	0.91 „

Mentzel finds the nutritive value of this fodder to be 1 : 14.5, but Troschke, considering the digestibility of the carbohydrates and oil to be 50 per cent., raises the nutritive value to 1 : 9.

No. 2 gave 1.086 per cent. of ash; this on analysis gave—

K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe.	Mn.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	SiO <sub>2</sub> .	CO <sub>2</sub> .
27.67	16.72	20.66	9.03	2.25	0.28	9.73	4.54	6.40	4.47
E. W. P.									

**Growth of Sugar-beet.** By B. CORENWINDER (*Bied. Centr.*, 1884, 113—115).—When beet was grown so that it should not receive any lime, the weight of the roots was barely one-half of those grown in presence of lime, although the weight of the leaves was doubled; the percentage of sugar was also lower, but not so the ash. It is remarkable that the absence of lime should have so great an effect on the growth of the plant, which under normal conditions contains only 0.037—0.04 per cent. of it. The author finds that water plants alone give trustworthy results when submitted to water culture; other plants should be grown in purified sand, to which the manures may be added.

E. W. P.

#### Preservation of Dried Washed Sugar-beet Mark Sections.

By H. HELLRIEGEL (*Bied. Centr.*, 1885, 93—98).—The sections having been exposed to different degrees of moisture and of temperature, it was found that they were not remarkably hygroscopic, in fact were less hygroscopic than many other foods, such as clover and meadow hay; moreover, they were not very liable to decomposition, and mildew did not form on them so readily as on oil cake and hay. After keeping for eight months, under very unfavourable conditions, they lost much less dry matter than rape or earth-nut meal, or clover and meadow hay do under similar circumstances.

E. W. P.

**Temperature of Hailstones.** By BOUSSINGAULT (*Ann. Chim. Phys.* [6], 3, 425—429).—In freshly fallen hailstones in the department of the Loire, the author has observed a temperature of —10.3°, while that of the surrounding air was 26°. Other observers have noted temperatures of —9°; —4°; and —2°.

R. R.

**Soil of Tunis.** By H. QUANTIN (*Ann. Agronom.*, **11**, 82–84).—The ten soils examined by the author are all poor in phosphoric acid, the percentages being 0·0065, 0·0408, 0·0084, 0·0572, 0·0416, 0·0168, 0·0462, 0·0136, 0·0105 and 0·1530. As the soils are light and calcareous, superphosphate or precipitated phosphate will probably prove to be the most advantageous manure. The proportions of nitrogen vary a good deal, and are as follows:—0·075, 0·090, 0·011, 0·165, 0·120, 0·143, 0·106, 0·157, 0·072, and 0·048 per cent. The use of sodium nitrate is recommended. J. M. H. M.

**Manurial Value of Freshly Fallen Leaves.** By EMMERLING and others (*Bied. Centr.*, 1885, 87–90).—Analyses of various leaves are given in the annexed table.

	Grey poplar ( <i>Populus canescens</i> ).	White willow ( <i>Salix alba</i> ).	Silver poplar ( <i>Populus argentea</i> ).	<i>Carpin. betulus</i> .	Silver birch ( <i>Betula alba</i> ).	Maple ( <i>Acer pseudo-platanus</i> ).	Red alder ( <i>Alnus glutinosa</i> ).	Oak ( <i>Quercus robur</i> ).	Reed beech ( <i>Fagus silvatica</i> ).
Water .....	20·88	20·27	18·31	17·03	15·73	17·74	17·06	17·73	15·35
Dry matter ....	79·12	79·73	81·69	82·97	84·27	28·26	82·94	82·27	84·65
In dry matter—									
Albumin .....	11·52	16·74	12·51	7·57	5·05	6·39	18·71	7·07	6·57
Fat .....	6·09	5·15	8·42	3·86	12·58	6·39	6·91	5·73	3·66
Carbohydrates ..	48·44	51·38	51·06	60·31	50·70	52·10	55·24	52·57	55·49
Fibre .....	26·44	19·72	20·46	24·83	29·10	28·31	15·74	30·68	29·82
Ash .....	7·51	7·01	7·55	3·43	2·57	6·81	3·40	3·95	4·46
N. in dry matter	1·843	2·681	2·001	1·212	0·808	1·022	2·993	1·131	1·052
K <sub>2</sub> O .....	14·79	21·60	20·31	10·96	12·73	14·30	7·87	12·92	10·55
Na <sub>2</sub> O .....	7·98	7·61	4·14	3·27	4·43	2·56	2·47	3·85	5·41
CaO .....	24·69	27·19	26·57	22·84	31·75	30·86	48·03	27·18	22·12
MgO .....	9·39	6·38	7·39	10·65	24·58	6·95	10·70	8·85	6·24
Fe <sub>2</sub> O <sub>3</sub> .....	1·08	3·02	1·28	4·66	2·71	1·04	3·58	2·07	1·78
Mn <sub>2</sub> O <sub>3</sub> .....	1·41	0·53	0·47	22·81	8·46	1·59	3·63	12·29	10·52
P <sub>2</sub> O <sub>5</sub> .....	4·97	7·56	5·37	5·84	3·18	2·44	5·53	4·08	4·72
SO <sub>3</sub> .....	5·07	13·37	8·46	4·31	3·81	3·10	5·76	3·48	3·85
SiO <sub>2</sub> .....	23·96	5·40	21·34	13·76	3·37	32·05	10·03	22·97	32·88
Cl .....	10·62	10·79	6·64	2·47	6·83	7·04	2·03	3·48	3·74
O equal to Cl ..	2·39	2·43	1·50	0·56	1·54	1·58	0·45	0·78	0·85

The manurial value of these leaves has been obtained by multiplying the nitrogen by 5, the phosphoric acid by 2, and the potash by 1, and then adding together the products; these manurial units (M.U.) are then multiplied by 10 pfennigs. In order to draw a comparison, the analytical figures above given have been reduced to a mean percentage of water (17·5), and the money value then calculated.

	Per cent. N.	Per cent. P <sub>2</sub> O <sub>5</sub> .	Per cent. K <sub>2</sub> O.	M.U.	Maximum value per centner in marks.
Grey poplar .....	1·52	0·31	0·92	9·14	0·91
White willow .....	2·21	0·44	1·25	13·20	1·32
Silver poplar .....	1·65	0·33	1·26	10·20	1·02
<i>Carpin betulus</i> .....	1·00	0·16	0·31	5·60	0·56
Silver birch .....	0·67	0·067	0·270	3·70	0·37
Maple .....	0·84	0·14	0·80	5·30	0·53
Red alder .....	2·47	0·15	0·22	12·90	1·29
Oak .....	0·93	0·13	0·42	5·30	0·53
Reed beech .....	0·87	0·17	0·39	5·10	0·51
Oat straw .....	—	—	—	—	0·50
Rye straw .....	—	—	—	—	0·35
Barley straw .....	—	—	—	—	0·45

Calculated on the dry substance, it appears that the fallen leaves of maple contain 4 per cent. of valuable matter (Na<sub>2</sub>O, K<sub>2</sub>O, CaO, MgO, P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>), and poplar and willow 5—5·7 per cent., whilst the rest only contains 2—2·3 per cent.; consequently the first three are constantly manuring the surface soil beneath their branches.

E. W. P.

**Manurial Value of Peat Waste and the Concentrated Liquors from Strontium-sugar Factories.** By MÄRCKER (*Bied. Centr.*, 1885, 140).—This manure contains 2·5—3·3 per cent. nitrogen, of which only 0·15—0·20 per cent. is derived from the peat, the rest of it comes from the roots in the form of nitrates, ammoniacal compounds, amides and amido-acids. The potash amounts to 11·5—14 per cent., and as it is unaccompanied by other salts which render the impure Stassfurt salts harmful, the mixture of peat and waste liquor is valuable.

E. W. P.



## Analytical Chemistry.

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**Modification of the Calcium Chloride Drying Tube used in Elementary Analysis.** By S. SCHMITZ (*Zeit. anal. Chem.*, **23**, 515—517).

**A Simple Fusion Salt.** By C. HOLTHOF (*Zeit. anal. Chem.*, **23**, 499—501).—Hydrogen sodium carbonate is recommended for the decomposition of silicates in place of sodium carbonate or the usual fusion mixture of potassium and sodium carbonates. It can easily be obtained pure, is not hygroscopic, and does not decrepitate when slowly heated. About 12 times as much hydrogen sodium carbonate as substance should be used and the mixture heated gradually to redness

or until the whole mass is fused. The crucible can be half filled with the mixture, so that much smaller crucibles can be used. S. R.

**Solubility of Glass.** By E. BOHLIG (*Zeit. anal. Chem.*, **23**, 518).—From experiments with numerous flasks, it was found that 100 c.c. of distilled water at the boiling temperature will in every two seconds extract as much alkaline silicate as will neutralise 0.1 c.c. of a solution containing 0.1 gram of oxalic acid per litre; with some old flasks and beakers no appreciable quantity was dissolved in the short time required for an ordinary quantitative analysis. S. R.

**The Absorption and Determination of Small Quantities of Hydrogen Sulphide in Gaseous Mixtures.** By OSMOND (*Bull. Soc. Chim.*, **43**, 70—71).—This is an improvement on Rollet's method for the examination of sulphur when present in small quantities. The mixture of hydrogen, carbonic anhydride, and hydrogen sulphide is passed through a series of bulbs each of which contains a certain quantity of silver nitrate solution of known strength. The hydrogen sulphide unabsorbed by the first bulb produces a precipitate in the second bulb and so on; thus by counting the number of bulbs the contents of which have been precipitated, the amount of sulphur present in the quantity of substance taken is at once determined. H. B.

**Nitrogen Determinations by Kjeldahl's Method.** By G. CZECHETKA (*Monatsh. Chem.*, **6**, 63—64).—In Kjeldahl's process for estimating nitrogen, the solution of the substance in strong sulphuric acid is oxidised by the addition of solid potassium permanganate. The author deems it advisable to substitute a saturated solution of permanganate in pure sulphuric acid for the solid salt. The reagent is not allowed to drop on the surface of the liquid under examination; the tap funnel containing the permanganate must dip under the surface of the solution. To avoid loss of ammonia, the caustic soda is poured through a Welter's safety tube into the flask containing the oxidised liquid, after the flask is connected with a condenser. An alcoholic solution of phenolphthalein is recommended as an indicator in titrating the ammonia. W. C. W.

**Estimation of Reverted Phosphoric Acid and of Phosphoric Acid in Dicalcium Phosphate.** By C. MOHR (*Zeit. anal. Chem.*, **23**, 487—491).—The sample (about 5 grams) is first digested three times with hot water, then heated for one hour at 60—70° with 25 c.c. of an alkaline ammonium citrate solution, the two filtrates mixed and diluted to 250 c.c. To 10—20 c.c. of this solution, an equal volume of fuming nitric acid is added, then the ammonium molybdate solution in excess, and the mixture allowed to remain for an hour at 85°; when cold, the precipitate is collected, and used for determining the phosphoric acid in the usual way. Numbers are given showing that this method yields results much nearer the truth than those of direct precipitation. S. R.

**Estimation of Graphite in Minerals.** By J. B. MACKINTOSH (*Chem. News*, 51, 147—148).—For the determination of graphite in minerals containing organic matter, carbonates, &c., the coarsely ground mineral is fused with potash, the fused mass dissolved in water, filtered through a Gooch's crucible, washed with water, dilute hydrochloric acid, and then with ammonia, thus leaving the graphite practically pure. D. A. L.

**Microscopic Analysis.** By HAUSHOFER (*Jahrb. f. Min.*, 1885, 1, Ref., 180—181).—*Cerium*.—When minerals containing cerium are treated with sulphuric acid, evaporated to dryness, and the residue dissolved in water with a little sulphuric acid, monoclinic crystals of cerium sulphate are first formed. If these crystals are dissolved in a larger quantity of water, hexagonal crystals of cerium sulphate are obtained. When dilute cerium solutions are precipitated by oxalic acid or ammonium oxalate, a curdy white precipitate is obtained, which becomes crystalline. It consists of prisms, pointed at both ends. From very dilute hot solutions, a salt is precipitated in rather large but very thin rhomboidal laminæ, the acute plane angle of which was found to be  $86^\circ$ .

*Yttrium and Thorium*.—For the detection of these metals, the sulphates,  $Y_2S_3O_{12} + 8H_2O$  (monoclinic) and  $ThS_2O_8 + 9H_2O$  (monoclinic) may be employed. The oxalates are, however, better suited for the purpose. When a drop of yttrium sulphate is diluted, and a drop of concentrated oxalic acid placed in contact with it, the distinct tetragonal oxalate is formed. The forms of erbium sulphate and oxalate coincide with those of yttrium. When a neutral solution of thorium sulphate is treated with dilute oxalic acid, the precipitate consists of hexagonal tablets, probably rhombic.

*Niobium and Tantalum*.—When a powdered niobium or tantalum mineral is fused with soda, and the residue treated with a little water, the sodium tantalate and niobate remain in the form of fine colourless straight prisms. If the sodium salt is dissolved in water containing soda, and diluted,  $Na_5Ta_6O_{19} + 25H_2O$ , separates first in hexagonal plates, and secondly as a salt resembling that obtained on treating the fused mass with water; it is probably sodium niobate. Tantallic and niobic acids dissolve slowly before the blowpipe in a bead of phosphoric acid. If the powdered glass is dissolved in 3 c.c. of hot water, and a few drop of this solution treated with soda on a watch-glass, prismatic crystals of sodium tantalate and niobate are formed. If some zinc-dust and two drops of sulphuric acid are added to the solution of the phosphoric acid bead, it assumes, after a short time, a fine sapphire-blue colour. B. H. B.

**Separation of Aluminium and Iron.** By P. VIGNON (*Compt. rend.*, 100, 638—639).—The solution is mixed with a large excess of concentrated trimethylamine and allowed to stand 24 hours. The iron is precipitated whilst the aluminium is completely redissolved. The precipitate after being washed with trimethylamine until the washings leave no solid residue on evaporation, is dried and ignited. The results are very accurate.

Trimethylamine redissolves chromic hydroxide in presence of ferric hydroxide, and probably this difference may also be utilised for the separation of these metals. C. H. B.

**Precipitation of Manganese with Bromine.** By C. HOLTHOF (*Zeit. anal. Chem.*, **23**, 491—498).

**Colorimetric Estimation of Manganese.** By OSMOND (*Bull. Soc. Chim.*, **43**, 66—69).—To the solution containing manganous chloride, metaphosphate of sodium in excess is quickly added, and subsequently lead dioxide. The solution acquires a violet colour from the formation of manganic metaphosphate, and this coloration is made a measure of the manganese present. The liquid may be filtered through paper. Tubes containing known amounts of manganic metaphosphate are used for comparison. The method is preferable to the gravimetric method in determining manganese in substances containing less than 4 per cent. The lead dioxide may be replaced by a current of ozonised oxygen. H. B.

**Estimation of Manganese in Spiegeleisen, Ferromanganese, &c.** By W. KAHLMANN and A. SMOLKA (*Monatsh. Chem.*, **6**, 65—74).—This process depends on the fact that a definite compound of manganese and oxygen is formed when manganese compounds are fused with a mixture of borax and potassium sodium carbonate. It is not applicable to the estimation of manganese in the silicate or in steel. The following reagents are required: (1.) Fusion mixture, prepared by fusing together 2 parts of borax glass with 3 parts of potassium sodium carbonate in a platinum dish. (2.) A solution containing 100 grams of ferrous sulphate per litre, acidified with 100 c.c. of pure sulphuric acid. (3.) A permanganate solution, of which 1 c.c. corresponds to 0.0025 gram Fe.

0.15 to 0.3 gram of the finely powdered substance is heated for 15 minutes in a platinum crucible over a Bunsen burner, and finally over a blowpipe. When the crucible is cold, the substance is mixed with 20 times its weight of fusion mixture, and the contents of the crucible kept in a state of fusion for 20 minutes. The lid is removed from the crucible and the mixture well stirred by means of a thick platinum wire for 15 minutes. The cold crucible lid and stirrer are transferred to a beaker containing 10 or 15 c.c. of the ferrous sulphate solution. To facilitate the solution of the fused mass, a small quantity of sulphuric acid is added. When solution is effected, the unoxidised iron is titrated with permanganate. The strength of the ferrous sulphate solution is determined by taking a second portion of 10 or 15 c.c., and directly titrating with permanganate.

6 atoms of manganese part with 5 atoms of oxygen, which will oxidise 10 mols. of FeO to Fe<sub>2</sub>O<sub>3</sub>, consequently 6 atoms of manganese correspond with 10 of iron. W. C. W.

**Analysis of Uranium Compounds.** By C. RAMMELSBURG (*Chem. Centr.*, 1884, 806).—Uranium is best separated from potassium, sodium, and lithium, by igniting the mixture and heating the alkaline

uranate thus formed with ammonium chloride in a current of hydrogen. The alkaline chlorides may then be extracted with water. Thallium can be precipitated by potassium iodide; barium, strontium, calcium, and lead by sulphuric acid. Barium carbonate cannot be advantageously used for precipitating uranium when magnesium and zinc are present, but may be employed for separating it from nickel and cobalt. Uranium is best separated from magnesium by precipitation with freshly prepared ammonium hydrosulphide in slightly acid solution, from manganese and zinc by the same reagent, in presence of excess of ammonium carbonate. Cadmium and copper are best separated by precipitation as sulphides in acid solution. L. T. T.

**Iodised Tannic Acid as a Reagent.** By O. SCHWEISSINGER (*Chem. News*, 51, 114).—A mixture composed of equal volumes of alcoholic solutions of iodine and tannic acid produces a transient rose coloration in dilute solutions of any salt having an alkaline reaction. With potassium carbonate the colour is perceptible, even with 1 per 1,000,000. Sulphates and chlorides do not disturb this reaction when present in small quantities. In strong solutions the rose is masked by a brown coloration. D. A. L.

**Apparatus for Collecting and Analysing the Gases Dissolved in Water.** By W. THORNER (*Chem. Centr.*, 16, 129—131, and *Rep. Anal. Chem.*, 5, 14—17).

**Estimation of Nitric Acid in Potable Water.** By MAYRHÖFER (*Chem. Centr.*, 1884, 848).—The method of estimating nitric acid in potable water, by means of indigo, is modified in the following way: Indigotin is rubbed up with 20—30 times its amount of pure concentrated sulphuric acid; after one day it is poured into water (1 gram indigo to 1.5 litre in water). After settling and filtering, the filtrate is diluted until 5 c.c. still give a persistent bluish-green colour with 5 c.c. of a potassium nitrate solution containing 0.0962 gram nitrate per litre. 5 c.c. of the indigo solution corresponds then with 60 mgrms. nitric acid per litre. A constant stream of the solution is run drop by drop into a mixture of 5 c.c. pure sulphuric acid and 5 c.c. of the water sample. Care must be taken not to have a momentary excess of indigo solution at any time. J. T.

**Calorimetric Estimation of Fuels.** By F. SCHWACKHÖFER (*Zeit. anal. Chem.*, 23, 453—476).—It is shown, in opposition to Bunte, that there is a relation between the theoretical and practical thermal values of a coal even when a small calorimeter is employed. The calorimeter described requires only 5—10 grams of the coal to be burnt in order to give accurate results. The combustion is effected in a stream of dry and pure oxygen, and the combustion-products are mixed with additional oxygen and led through a layer of heated sugar-charcoal to render the combustion complete. The amount of water is so regulated that the temperature does not rise more than 10° C. with 5—6 grams of mineral coal and 2—4 grams of sugar-charcoal. To check the results obtained, the thermal value is calculated from the

percentage combustion of the coal, by the following modification of Dulong's formulæ:—

$$\text{No. of calories} = \frac{(8080 \times \text{p. c. of C}) + (34,462 \times \text{p. c. of H}) - (621 \times \text{p. c. of water})}{100}.$$

A comparison between the numbers, shows that the result calculated from Dulong's formula is in all cases lower than that obtained by the direct method.

The gases formed contain from 0·2—0·8 per cent. of carbonic oxide, and the total volume amounts to about 30 litres. The gas is analysed and the sum of the products of the rise in temperature in degrees C. by the heat capacities (weight  $\times$  sp. heats) of each of the gases, gives the number of calories contained in the gases. A correction must be made for the air in the apparatus at the commencement and also for the free oxygen. Finally, the calorimetric value of the sugar-charcoal has to be deducted from the total, the difference being the calorimetric value of the coal. S. R.

**Detection of Sulphuric Acid in Wine.** By P. FERRARI (*Chem. Centr.*, 1884, 184).—To detect free sulphuric acid occurring with acid and normal sulphates in wine, 20 c.c. of the liquid are shaken up with a mixture of equal volumes of alcohol and ether in an 80 c.c. flask. After 24 hours, the liquid is thrown on to a filter moistened with the alcohol-ether mixture, and the precipitate washed in the flask with the mixture until its reaction is neutral. The precipitate, consisting exclusively of normal sulphates, is dissolved in hot water, and the sulphuric acid is precipitated by barium chloride. The alcohol-ether filtrate is distilled, the residue is taken up with water, and the sulphuric acid in it determined; only a part of this is to be reckoned as free sulphuric acid, as a portion has come from the conversion of acid sulphates into normal sulphates and free acid. Since the acid formed from the acid sulphate and that from the normal sulphate are equal in quantity, the difference between the two sulphuric acid estimations is to be reckoned as free sulphuric acid. J. T.

**Wine Analysis.** By R. ULBRICHT (*Chem. Centr.*, 1884, 684).—To detect sulphurous acid, salicylic acid, and metals in wine and must, the author proceeds as follows:—100 c.c. wine or 50 c.c. must and 50 c.c. water are distilled, and the distillate is collected in a receiver containing 5 c.c. of a solution, of which 1 litre contains 5 grams iodine and 7·5 grams potassium iodide. After 10 c.c. are distilled over, the contents of the receiver are tested with some drops of hydrochloric acid and barium chloride. Without interrupting the distillation, the next fraction is collected in a receiver containing a drop of ferric chloride. If the sample contains only 0·03 gram salicylic acid per litre, the well-known reaction immediately appears. The distillation is continued until 50 c.c. has passed into the second receiver. The residue can be tested for metals by hydrogen sulphide, &c. J. T.

**Determination of Non-volatile Residue in Wines, &c., by Evaporation in a Vacuum.** By J. PETER (*Bull. Soc. Chim.*, 43, 71—74).

**Detection of Saccharose in Wine.** By MEDICUS (*Chem. Centr.*, 1884, 852).—In some genuine wines, the sugar was determined first directly, and again after boiling with hydrochloric acid. In the second estimation, invariably a little more sugar was found (by Allihn's modification of Soxhlet's method) than in the first. Since this might be due to a gum-like substance, 100 c.c. were evaporated to one-fourth, and treated with alcohol, when a gummy deposit formed on the sides of the vessel. This was dissolved, inverted, and treated as for sugar. The amount of copper precipitated agreed tolerably well with the difference found above. J. T.

**Estimation of Sugar and Glucose.** By L. BATTUT (*Chem. Centr.*, 1884, 687—688).—Circumstances occur in sugar-making in which the polarimeter cannot be applied; in such cases recourse must be had to the copper solution. The author, after a comparison of various methods, prefers the application of Pellet's solution, care being taken to work always with the same volume and same amount of sugar. J. T.

**The  $\frac{4}{5}$  Method of Sugar Analysis.** By P. CASAMAJOR (*Chem. News*, 51, 145—146).

**Composition of Starch Syrup, of Honey, and its Adulteration.** By J. SIEBEN (*Bied. Centr.*, 1885, 134—137).—Starch-sugar syrup yields less alcohol when fermented than pure dextrose, but more than corresponds with the dextrose supposed to be in the syrup; the residue, after fermentation of pure dextrose, will not reduce Fehling's solution, whilst the residue from dextrose syrup reduces it strongly. The composition of the syrup is thought to be:—Dextrose 21·97 per cent., maltose 15·80, dextrin 41·96, water 20·10, ash 0·30.

After examining many samples of honey, the author finds that saccharose is sometimes present to the amount of 4 per cent. (in one case 8 per cent.); the ratio of lævulose to dextrose varies, the total quantity being 68—78 per cent. The following represents the average composition of 60 samples:—Dextrose 34·71 per cent., lævulose 39·24, saccharose 1·08, water 19·98, non-saccharine matter 5·02. Lævulose of honey is more readily turned brown by hydrochloric acid than dextrose. To test honey for adulteration with starch-syrup, 25 grams honey and 12 grams yeast (free from starch) are dissolved in 200 c.c. water. After 48 hours' fermentation and addition of aluminium hydroxide, it is made up to 250 c.c.; 200 c.c. are then evaporated down to 50 c.c. and polarised. If any starch-sugar is present, the liquid will be dextro-rotatory, for the other constituents yield only lævorotatory, or else neutral products. The residue, after fermentation, is heated with a little hydrochloric acid, when there should be no reaction on Fehling's solution, as honey produces no dextrin. Two other methods are mentioned, but not described. E. W. P.

**Polarimetric Estimation of Sugar in Milk.** By M. SCHMÖGER (*Bied. Centr.*, 1885, 129—130).—After coagulating 100 c.c. of milk by 6 c.c. of 15 per cent. acetic acid, and then boiling the whey with

3—4 c.c. of a solution of lead acetate (sp. gr. 1.2), the lactose is estimated in the clear filtrate by the polariscope. Another method is to add 5 c.c. of phosphotungstic acid to the whey and filter. A third method is a modification of Hoppe-Seyler's process, in which after 50 c.c. of milk are decomposed by lead acetate, 5 c.c. of a 10 per cent. solution of alum are added before making up to 100 c.c. All three methods give results not agreeing very accurately with one another, nor with that obtained gravimetrically. The methods of Soxhlet and others are accurate so long as the lactose is pure, but inaccuracies appear as soon as milk is operated on; the author believes that these differences are due to the existence of some carbohydrates in the milk, such as Ritthausen has hinted at. E. W. P.

**Influence of the Lead Precipitate on Polarisation.** By F. SACHS and R. DE BARBIERI (*Chem. Centr.*, 1884, 902—903).—The authors found that the precipitate of basic lead acetate had no noticeable influence on the polariscopic estimation of osmose-waters or molasses, but that it became a source of error in the estimation of sugar-cane juice, as in this case the percentage of sugar shown increases with the bulk of the precipitate. They then made a series of experiments with solutions of pure sugars, to which potassium citrate, tannin, sodium oxalate, chloride or carbonate, or potassium sulphate had been added, and estimated the sp. gr., weight, and volume of the precipitate caused on the addition of lead acetate, and the influence on the polariscopic readings. Only in the case of tannin was the increase of bulk such as exactly to correspond with the change of reading. This the authors believe to be due to the presence of sodium or potassium acetate in the other cases, which prevents the lead precipitate carrying down sugar with it. They, therefore, consider that in the analysis of sugar-juice the whole bulk of the precipitate should be taken into account, and that both in the analysis of juice and of molasses the employment of tannin is to be avoided.

L. T. T.

**Trannin's New Saccharimeter.** (*Dingl. polyt. J.*, 255, 293. From *Bulletin de la Société Industrielle de Nord de la France*, 1884, 107).—In this apparatus the various parts are arranged in a vertical position. D. B.

**Phenols as Reagents for Carbohydrates.** By A. IHL (*Chem. News*, 51, 114—115).—In all these experiments, an alcoholic solution of the phenol was mixed with the finely powdered carbohydrate and hydrochloric acid and cautiously heated. Cane-sugar with  $\alpha$ -naphthol gives a red-violet coloration, which disappears on adding water; with  $\beta$ -naphthol a yellow colour, which on prolonged boiling changes to dark greenish-yellow, with greenish fluorescence; with resorcinol an intense fiery red, and with pyrogallol a fine red colour, both colours being permanent with water; phloroglucol gives with cane-sugar an intense yellow-red colour, which on addition of water becomes light yellow. *Milk-sugar* gives a violet colour with  $\alpha$ -naphthol, yellow with  $\beta$ -naphthol, and red-brown with phloroglucol. Dextrin gives a blue colour with  $\alpha$ -naphthol, yellowish with  $\beta$ -naphthol, and dirty yellow



with phloroglucol. Glucose gives a yellowish-green coloration and strong green fluorescence with  $\beta$ -naphthol, and yellowish-red with phloroglucol. Arabin yields a red colour with  $\alpha$ -naphthol, light yellow with  $\beta$ -naphthol, a cochineal-red dye, permanent with water with phloroglucol, whilst starch gives a deep reddish-violet with  $\alpha$ -naphthol, and a faint yellow with  $\beta$ -naphthol. The last five carbohydrates all give yellowish-red colours with resorcinol and with pyrogallol.

D. A. L.

**Detection of Chloral.** By CASALI (*Chem. Centr.*, 1884, 198—199).—Milk containing chloral was examined as follows:—The milk was vigorously and repeatedly shaken with twice its volume of ether and concentrated aqueous potash, then allowed to stand for some time. The upper ethereal layer, which was light yellow, and only very slightly turbid, was removed, and the aqueous solution treated again with ether. The two ethereal solutions were filtered and distilled at 45°. To detect the chloral hydrate in the distillate, a part was taken and mixed with one-third of its volume of water, and the ether allowed to evaporate. Some drops were added to an ammoniacal solution of silver oxide previously warmed, a silver mirror immediately appeared. A few drops also reduced Fehling's solution. A portion of the distillate was mixed with twice its weight of alcohol, and burnt in a lamp with an asbestos wick, under a bell-jar. The smoking wick smelled strongly of chloral hydrate and chloroform; a rod moistened with ammonia became covered with white needles when placed in the bell-jar; the water condensed in the jar had an acid reaction, and gave a precipitate with silver chloride. The same results were obtained when light petroleum was substituted for ether. The author considers no difficulty would be met with in applying the method to food, drink, medicines, and the contents of the stomach.

J. T.

**Estimation of Milk Fat.** By L. LIEBERMANN (*Zeit. anal. Chem.*, 23, 476—486).—The author refutes Wolf's criticism (*Zeit. anal. Chem.*, 23, 87) on the accuracy of his volumetric method for estimating fats (*Abstr.*, 1884, 372). The modification of the process which is now adopted consists in mixing 50 c.c. of the milk with 50 c.c. of potash solution of sp. gr. 1.27, then, after five minutes, adding 50 c.c. of aqueous ether. The mixture is shaken, and 20 c.c. of the ether withdrawn by a pipette, and evaporated to dryness. It is best to dry for half an hour at 110°, or to heat over a small gas flame until the smell of decomposed butter is detected. The areometric method of Soxhlet should be used if this method is inapplicable.

S. R.

**Tests for Butter.** By J. ZANNI (*Chem. Centr.*, 1884, 63—64).—I. A small quantity of the butter to be tested is heated in a porcelain vessel to 130°, allowed a day to cool, and then strongly kneaded with a glass spatula. Artificial butters thus treated have an odour of tallow, which is not the case with genuine butter, even if several months old. II. 2 grams of genuine butter give 0.012 gram of ash as a maximum, oleomargarin, &c., give 0.025—0.036 gram.

III. Added butyric acid is detected by comparing the quantity of acid extracted by washing with water with that of the volatile acids obtained by the processes of Hehner, Anghell, or Reichert. IV. Pure butter when examined under the microscope at 26—30° appears formed of regular transparent spherical nodules. When adulterated with vegetable oils, butter begins to lose this appearance at 18—24°. Margarin, &c., show a more or less crystalline structure. V. Adulteration with vegetable oil may be detected by the smell if a small quantity of the butter is well rubbed up in the palm of the hand. VI. No genuine butter contains more than 53 per cent. oleic acid. A good butter should contain from 87·5—88 per cent. of insoluble fatty acids.

L. T. T.

**Tests for Butter and Butterine.** By J. HORSLEY (*Chem. News*, 51, 114).—When two test-tubes, containing respectively a piece of butterine and a piece of pure butter, equal in size, are held in the palm of the hand (or heated at 98° F.), the butter takes twice as long to melt, and is never as clear and oily as the butterine. Addition of alcohol to the ethereal solution of butter causes a voluminous white precipitate to form, whereas with butterine no such reaction is obtained.

D. A. L.

**Toilet Soap Analysis.** By E. VALENTA (*Chem. Centr.*, 1884, 199—200).—*Water*.—4 to 5 grams of the soap are heated at 60—90° for 3—4 hours, then some hours at 100°, and finally at 120°. *Alcohol*.—In the case of the transparent, so-called glycerine, soaps, 50 to 60 grams mixed with coarse pumice powder are distilled in a retort; for a considerable time the temperature is kept at 110°, finally it is raised to 120°. The amount of alcohol found is deducted from the water. *Ash*.—5 to 10 grams are burnt in small portions in a platinum crucible; the ash may reach 20 to 35 per cent. The ash is examined for sodium silicate. In its absence, the amount of alkali that was combined with fatty acids is estimated by titrating the aqueous extract of ash with standard acid; otherwise the total alkali, silica, chlorine, and sulphuric acid must be determined, or an estimation of the carbonic anhydride must be made. *Fatty acids*.—5 to 10 grams are heated in a capacious dish with dilute sulphuric acid (1 : 15) until the fatty acid floats on the surface as a clear oil. A weighed quantity (5 to 10 grams) of previously fused stearin or wax is now added, so as to solidify the separated acids after cooling. The cake obtained is repeatedly melted with water, fused on the water-bath in a platinum dish, and allowed to cool. After drying in a vacuum, it is weighed. The weight found, after deducting the stearin added, may be taken as fatty acid hydrate, or 3·25 per cent. may be deducted to obtain the anhydrous acids. Otherwise 20 to 30 grams of soap may be treated as above, and the fatty acids filtered through a moist paper, washed well, dried at 100°, and finally in a vacuum, and weighed. The fusing point, &c., may then be determined. *Glycerol*.—5 to 10 grams of the soap are decomposed with sulphuric acid, filtered, washed with a little warm water, and the filtrate evaporated, after neutralisation with sodium carbonate. The dry residue is extracted with ether alcohol (1 : 5), and the

extract is evaporated at the lowest possible temperature, finally dried over sulphuric acid, and weighed. J. T.

**Testing Oil of Cassia.** By G. HEPPE (*Chem. Centr.*, 1884, 910—911).—Hager's method of testing, by shaking the oil of cassia with its own volume of light petroleum, is satisfactory in most cases; but if the adulterant is copaiva resin, it is not extracted by this method. Such an adulterated oil also dissolves in 80 per cent. alcohol and in glacial acetic acid to a clear solution, although the resin alone is insoluble in acetic acid. L. T. T.

**Valuation of Indigo.** By C. RAWSON (*J. Dyers and Colourists' Soc.*, 1885, 74—81).—The object of the research was to devise some method whereby the exact composition of indigo, so far as its tinctorial power was concerned, might be determined, as mere inspection of the sample is apt to produce an error of 3*d.* to 9*d.* per lb. Moreover, many of the methods recommended in text-books are utterly untrustworthy, and the opinions concerning the degree of solubility of indigo in sulphuric acid, as stated by various writers, are very diverse. After repeated experiments, the author has adopted the following as the most trustworthy and rapid method: 1 gram of finely powdered indigo is mixed with its own weight of ground glass; this mixture is carefully added during constant stirring to 20 c.c. of sulphuric acid (sp. gr. 1·845) contained in a cylindrical porcelain crucible (capacity 1½ oz.), the whole is then heated in an oven for one hour at 90°, and the sulphindigotic acid afterwards diluted, and made up to 1 litre. There appears to be no advantage in heating for any longer period. To estimate the indigotin present in the filtered solution, the permanganate process is preferred, as by the use of chlorine or potassium dichromate, the results are always too high; the poorer the quality of the sample the greater will be the error, nor is the permanganate process free from error, but that error can to some extent be eliminated. Bleaching powder, potassium chlorate and dichromate, are unsatisfactory, for the indigo solution must be of such a strength that, in the case of inferior qualities, the end of the reaction is obscured by the dark colour of the liquid. When, therefore, a sample is to be estimated as easily and rapidly as possible, and with accuracy, the permanganate process is to be used: 50 c.c. of the solution of sulphindigotic acid are taken and diluted to 250 c.c., and then titrated with potassium permanganate (0·5 gram per litre), the end of the reaction, the change to light yellow, being clear and distinct; 316 parts permanganate = 655 parts indigotin. The other constituents of raw indigo, namely, indigo-brown, -red, and -gluten, are also affected by oxidation, and experiments have been made to ascertain to what extent the action affects the estimation of pure indigotin. Medium quality indigo was treated with hydrochloric acid, alcohol, and sodium hydroxide, and the extracts evaporated to dryness, dissolved in sulphuric acid, diluted and filtered, and then submitted to oxidation. The alcoholic extract consisted principally of indigo-red, but a small quantity of brown was present as shown by the formation of a brown precipitate when water was added; the red is acted on by perman-

ganate in a manner similar to indigotin. The sodium hydroxide extract consisted of indigo-brown; it was dissolved in acid, but was precipitated on adding water; on this compound, permanganate had but little action. The hydrochloric acid extract contained indigo-gluten, resinous substances, and mineral matter, notably ferrous salts; the amount of permanganate required to oxidise this solution varied with the quality of the original sample. Now as indigo-red is no impurity, and indigo-brown has no action, it is evident that the inaccuracy of the process is due to the presence of substances soluble in hydrochloric acid. To eliminate this error, the following method has been devised. The 50 c.c. of the filtered solution of indigo are first mixed with 50 c.c. of water and 32 grams sodium chloride; after remaining for two hours, the precipitate of sodium sulphindigotate is filtered off and washed with 50 c.c. of sodium chloride solution (sp. gr. 1.2), after which it is dissolved in hot water, cooled, mixed with 1 c.c. sulphuric acid, diluted to 300 c.c., and titrated; a correction of 0.0008 c.c. must be introduced to allow for the sulphindigotate dissolved in the salt solution.

The employment of Ullgren's method (this Journal, 1865, 217) is not altogether satisfactory, the results being too high. Müller's process (*Amer. Chemist*, 5, 128) is very accurate, but the author has somewhat modified it with advantage. The solution of sodium hyposulphite is prepared by placing some zinc in a 100 c.c. flask, and adding a solution of sodium hydrogen sulphite (sp. gr. 1.30). The flask is then corked, and allowed to remain until there is no longer an odour of sulphurous anhydride, after which the liquid is decanted and diluted with 5 litres water, containing 0.05 gram of calcium hydroxide in suspension; after subsidence, the clear liquid is syphoned off and stored; to prevent oxidation, 50 c.c. of petroleum is added; to further prevent change, the bottle is covered with black paper; to remove the liquid, a syphon tube is introduced into one perforation of the cork, whilst another perforation admits of connection with a coal-gas supply. For the standardising of this solution, a modification of Bernthsen's process (*Abstr.*, 1881, 310) is used. Standard copper sulphate is prepared by dissolving 1.904 grams of the crystallised salt (= 1 gram indigotin) in 1 litre water containing 100 c.c. of ammonia (0.880); of this mixture 50 c.c. are then boiled to expel air and cooled. The flask in which the titration is performed is provided with a perforated stopper to admit a burette containing indigo-carmin as indicator, another burette for the hyposulphite so arranged that only coal-gas or hydrogen shall have access to the liquid, and an exit and inlet tube for admission of gas to the mixture in the flask. Hyposulphite is run in until the copper solution is nearly colourless, when a few drops of carmine are added, and then a further quantity of hyposulphite until a brownish-red colour is assumed—the end of the reaction is sharp; the quantity of the hyposulphite required to decolorise the carmine is very small, but it must be previously determined. One molecule of ammoniacal copper solution is decolorised by the same quantity of hyposulphite, as one molecule of indigotin dissolved in sulphuric acid, so that using the above quantities, 50 c.c. of copper sulphate are equivalent to 0.05 indigotin, so that supposing

25 c.c. of sodium hyposulphite have been run in, each c.c. will correspond with 0.002 indigotin. To prepare the indigo sulphate for titration, the indigotic acid, as previously described, is diluted to 1 litre; of this 50 c.c. are boiled and cooled; solutions of indigotin and better qualities of indigo are pale yellow when reduced, but if the quality is low, the final solution is brownish-yellow. As hyposulphite has no action on indigo-red, -brown, or -gluten, this last process gives the percentage of indigotin only; but if iron is present in the ferric state then the results are too high, for hyposulphite reduces ferric salts to ferrous, but the quantity required is exactly the same as that required to reduce the copper solution; it is only in low class indigo that there is much iron, and then it is chiefly in, or is subsequently reduced to, the ferrous condition.

The sublimation process as worked by Crum and Lee (Abstr., 1884, 1438) is stated by the authors to be satisfactory, but Rawson thinks otherwise, for although estimations of one sample made under one cover may agree, yet if another cover is employed, a difference of 2 per cent. may be found; he has also found that the other constituents of indigo are more or less affected by sublimation, and that pure indigotin is partly decomposed, leaving a brown residue amounting to 10 per cent. of the whole; with inferior samples, the results are too high, whilst with samples rich in indigotin the results are too low.

Amongst the methods of estimating indigotin by reduction, Crace-Calvert's method of reduction by ferrous sulphate and sodium hydroxide has been thoroughly examined. The process now proposed for general practice is to mix 1 gram of finely powdered indigo with 2 grams ferrous sulphate, 5 grams sodium hydroxide and 1 litre water in a flask closed by a cork with three perforations, one for a syphon, the other two for a constant supply of hydrogen; the mixture is kept at a little below boiling point for  $1\frac{1}{2}$ —2 hours, when 500 c.c. of the clear liquid are syphoned off, and allowed to oxidise; excess of hydrochloric acid is then added, and the precipitate well washed with hot water; the indigo-brown and -red are removed by hot alcohol, and the pure indigotin dried at  $100^{\circ}$ . Finally Rawson describes a new method devised by himself, and recommends it as being very accurate and rapid. One gram of finely powdered indigo is ground to a thin paste with water, and introduced into a flask with 500—600 c.c. lime water; the cork of this flask is fitted with tubes as in the previously described method. The liquid is heated to  $80^{\circ}$ , and to it is added 100—150 c.c. of sodium hyposulphite (five times stronger than that already described), when it assumes a yellow colour, after which it is heated nearly to boiling for half an hour; after subsidence 500 c.c. are syphoned off into a conical flask when oxidation ensues. After complete oxidation excess of hydrochloric acid is added, and the precipitate of indigotin and indigo-red is filtered off, and the red removed by alcohol. The principle of this method has been applied to a volumetric process, but the results at present are not satisfactory enough to warrant publication.

E. W. P.

**Valuation of Hay by Chemical Analysis.** By A. MAYER (*Ann. Agronom.*, 11, 90—93).—The author demonstrates the mis-

leading character of the ordinary chemical analysis as a guide to the nutritive or market value of samples of hay, and declares that a simple botanical analysis, giving to each species the value assigned by long experience, is far preferable. As an example he cites four samples of hay, sold at the following prices:—(1) Frisian hay 20 florins per 500 kilos.; (2) hay from L'Yssel, 18 florins; (3) blue hay from La Lende, 11 florins; (4) inferior hay from marshy soil, 6 florins. The ordinary chemical analysis of these samples yielded the following results:—

	No. 1.	No. 2.	No. 3.	No. 4.
Water .....	9.1	9.2	9.4	10.2
Albuminoids .....	8.8	9.3	10.2	7.1
Ether extract.....	3.1	2.5	2.8	1.3
Soluble carbohydrates.	42.9	40.8	42.8	42.5
Crude fibre.....	29.0	29.5	30.2	33.0

Regarding as is usual, the albuminoids as worth double as much as the ether extract (fat) and four times as much as the soluble carbohydrates, the following proportional values are arrived at:—No. 1, 20 florins; No. 2, 19.77 florins; No. 3, 21.28 florins; and No. 4, 17.17 florins. Thus No. 3 appears by chemical analysis to be worth more than No. 1, although it can be bought at half the price. Botanical analysis of the same four samples discloses the following species:—the dominant species in each sample being italicized.

No. 1.		No. 2.	
Grasses :	<i>Anthoxanthum odoratum</i> . <i>Agrostis vulgaris</i> . <i>Poa trivialis</i> . <i>Holcus lanatus</i> . <i>Cynosurus cristatus</i> . <i>Glyceria maritima</i> .	Grasses :	<i>Poa trivialis</i> . <i>Festuca elatior</i> . <i>Glyceria maritima</i> . <i>Cynosurus cristatus</i> . <i>Bromus mollis</i> . <i>Hordeum secalinum</i> .
Leguminosæ :	<i>Trifolium pratense</i> .	Leguminosæ :	<i>Trifolium minus</i> .
Weeds :	<i>Agrostis alba</i> . <i>Ranunculus repens</i> . <i>Lychnis flos-cuculi</i> . <i>Veronica serpyllifolia</i> . <i>Cerastium glomeratum</i> . <i>Alopecurus geniculatus</i> . <i>Hordeum murinum</i> . Moss (hypnum).	Weeds :	<i>T. pratense</i> . <i>Agrostis alba</i> . <i>Ranunculus repens</i> . <i>Plantago lanceolata</i> . <i>Carex vulpina</i> . <i>Crepis virens</i> . <i>Cerastium glomeratum</i> .
No. 3.		No. 4.	
Grasses :	<i>Poa fertilis</i> . <i>Anthoxanthum odoratum</i> .	Grasses :	<i>Anthoxanthum odoratum</i> .
Weeds :	<i>Agrostis canina</i> . <i>Triodia decumbens</i> . <i>Molinia cœrulea</i> . <i>Phragmites communis</i> . <i>Carex</i> (several). <i>Salix repens</i> . <i>Cirsium palustre</i> . <i>Potentilla tormentilla</i> .	Weeds :	<i>Juncus</i> (several). <i>Carex</i> (several). <i>Equisetum limosum</i> . <i>Sphagnum</i> . Other mosses. <i>Scutellaria galericulata</i> . <i>Comarum palustre</i> . <i>Lychnis flos-cuculi</i> . <i>Galium palustre</i> . <i>Polystichum thelypteris</i> .

Two species of the best and two of the worst of the plants enumerated above were submitted to analysis with the following results:—

	Crude protein, N $\times$ 6.25.	Albumin.	Nuclein.	Digestible albuminoïds.
<i>Anthoxanthum odoratum</i> ..	10.8	8.2	6.1	4.7 p. c.
<i>Poa pratensis</i> .....	8.5	6.5	4.8	3.7 „
<i>Equisetum hyemale</i> and <i>arvense</i> .....	20.0	15.6	7.8	12.2 „
<i>Carex vulgaris</i> .....	14.6	12.2	8.4	6.2 „

The nucleïn, or indigestible nitrogenous matter, was estimated by Stutzer's process of artificial digestion; the albumin by copper hydroxide. These chemical results again are in contradiction with the values given by experience. There may be deleterious substances in the weed grasses and other plants which detract from their theoretical nutritive value.

J. M. H. M.

**Separation of Alkaloids in Forensic Analysis.** By H. BECKURTS (*Chem. Centr.*, 1884, 905).—By the following method, the employment of amyl alcohol in the separation of morphine and narceine may be avoided. The mass to be investigated is extracted with spirit acidified with oxalic acid and the united extracts treated as usual. After shaking out with ether, the acid solution is exactly neutralised with lime- or baryta-water and washed with ether. The washed liquid is filtered, and the precipitate—which consists of calcium (or barium) oxalate, together with any morphine or narceine present—is dried and extracted with boiling alcohol. This solution on evaporation leaves the morphine and narceine in a much purer state than when amyl alcohol is employed.

L. T. T.

**Pepper Powder.** By W. LENZ (*Zeit. anal. Chem.*, 23, 501—513).—Satisfactory determinations of the purity of samples of pepper cannot be made by extraction with various solvents, as the employment of different forms of extraction apparatus will give entirely different results. For example, a sample of pepper when treated with light petroleum for 12 hours in a Soxhlet's apparatus gave 1.98 per cent. of extract, whilst with Tollens' apparatus in 11 hours as much as 4.55 per cent. was obtained. This is due to the higher temperature of the light petroleum in the last-named apparatus as well as to differences in the construction of the two forms of apparatus. It has been recently proposed (*Pharm. Centr.*, 24, 566) to strew the pepper on a strong aqueous solution of iodine. In this way the pepper is coloured blue and palm-nut powder yellow, and the larger particles can be separated mechanically. The author confirms the usefulness of this method. As pepper is characterised by its large amount of starch as compared with that in its common adulterants, the only trustworthy method for a quantitative estimation is to convert the contained starch by boiling with dilute hydrochloric acid and to determine the sugar formed by means of Fehling's solution.

The mean amounts of sugar obtained from the dry substances (calculated as free from ash) are:—Black pepper, 52 per cent.; white pepper, 60 per cent.; palm-nut powder, 22.6 per cent. (free also from

fat) ; pepper husks, 16.3 per cent. No pepper if pure should give less than 50 per cent. of sugar when calculated in this way upon the dry substance freed from ash. The percentage of palm-nut powder contained in the pepper can be approximately calculated by subtracting the percentage of sugar from 52 and dividing the product by 0.29.

S. R.

**Detection of Sugar in Urine.** By C. GIACOMO (*Chem. Centr.*, 1884, 185).—In testing urine for sugar with copper solution, the blue coloration frequently disappears and passes into yellow. The author finds that neither colouring matter, gum, albuminoid nor extractive matters cause this change, as after their removal by means of animal charcoal and lead acetate the sugar reaction sometimes fails; if, however, an alcoholic extract of the urine extract is treated with concentrated alcoholic zinc chloride, filtered and evaporated after 48 hours, then the presence of sugar will be indicated by the copper solution. It is the creatinine, so removed, which prevents the reduction of the copper salt by the sugar, as it reduces the copper salt and combines with the cuprous oxide produced to form a white granular powder, soluble in ammonia and alkalis. This reaction is so delicate that  $\frac{1}{100000}$  of creatinine can be detected. The sugar reaction only takes place when all the creatinine present has combined with cuprous oxide, so that in presence of creatinine a larger quantity of copper sulphate is required, and Trommer's test requires to be so modified that 10—12 drops tartaric acid, much copper sulphate, and an excess of potassium hydroxide are added to the urine.

J. T.

**Estimation of Dextrose in Urine by Means of the Soleil-Ventzke Polarimeter: Lævorotary Substances in Urine.**

By W. MÜLLER (*Pflüger's Archiv*, 35, 76—108).—The author has examined a very large number of urines both with the polarimeter and by titration with Fehling's solution, and confirms the non-agreement between the two methods, to which attention has several times been drawn. The result is to show that in most cases less sugar is indicated by the polarimeter than by Fehling's solution. The presence of lævulose having been suggested as a cause of the discrepancy, this substance was sought for, but with negative results. The author's experiments finally led to the conclusion that a lævorotary substance of an acid nature was present in many diabetic urines, and experiments on the isolation of the substance were in progress when he became aware of Kulz's discovery of pseudo-hydroxybutyric acid in the urine in some severe cases of diabetes (this vol., p. 284), and therefore abandons his researches on the subject.

A. J. G.

**Sources of Error in the Titration of Carbamide with Mercuric Nitrate.**

By H. BRAUN (*Pflüger's Archiv*, 35, 277—294).—In this titration (when neutralisation is not resorted to during the titration) the author finds that Liebig's correction does not lead to correct results. For solutions containing more than 0.2 gram per 10 c.c., however, fair results can be obtained by adding 0.1 c.c. for every additional c.c. above 20 of mercuric nitrate required per 10 c.c.



of carbamide solution. It is necessary that the whole volume of the mercury nitrate should be run in at once; a slow titration gives discordant results. The presence of free nitric acid appears to still further increase the rise of the amount of mercuric nitrate used with the increase in the amount of carbamide solution. A. J. G.

**Chemistry of Urine.** By H. SPIELHOFF (*Chem. Centr.*, 1884, 851). —The author has experimented with Ehrlich's diazo-reaction, and has ascertained that urine which gives no reaction with the normal solution gives only a pseudo-reaction with stronger solutions, and not the true froth colour and green precipitate. A red coloration is always accompanied by a green precipitate; the application of concentrated diazo-solutions are to be avoided. The author found that diazo-benzenesulphonic acid can be used to detect ethyl acetoacetate in urine. A strong solution must be employed. Equal quantities of urine and the reagent are mixed, and saturated with ammonia, not with potash. If a red coloration appears, a small quantity of the mixture is treated with hydrochloric acid, when a violet coloration should be obtained. The rest of the urine mixture is treated with a large excess of ammonia or potash, when a distinct red colour is obtained even when largely diluted. J. T.

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## Technical Chemistry.

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**Behaviour of the Haloid Compounds of Silver to the Solar Spectrum. Action of Dyes and other Substances in increasing the Sensibility of the Salts.** By J. M. EDER (*Monatsh. Chem.*, **6**, 1—47).—This paper contains several diagrams which indicate the degree of sensitiveness to various portions of the solar spectrum, exhibited by dry gelatin plates prepared with different physical modifications of silver bromide, silver iodide and chloride, and also with mixtures of bromide and chloride and iodide. The action of a large number of dyes in increasing the relative sensibility of the plates to different coloured rays of light is also shown by diagrams.

The author confirms Abney's observation that a mixture of silver bromide and silver iodide gelatin emulsion exhibits two maxima of sensitiveness, and he also confirms Schumann's statement that the two separate maxima are merged into one when the mixed emulsion is digested for an hour. The sensitiveness of such an emulsion is greater for the less refractive rays than that of pure silver bromide. The best results are obtained with silver bromide containing 5 per cent. of silver iodide.

Hofmann's violet and other commercial violets increase the sensitiveness of the plates to orange, yellow, and green rays. Iodine green is the best sensitiser for the ultra-red. Cyanin is very good for orange and red. The total sensitiveness to white light is only one-tenth or one-fifth that of uncoloured plates, but the relative sensi-

tiveness for orange is increased a hundredfold. With these plates a dull, dark red light should be used.

The eosin colours are good sensitisers for green, yellowish-green, and yellow, but not for red. A mixture of cyanin and eosin yields excellent results.

The sensitiveness of an ordinary silver bromide gelatin plate is increased by immersion in ammonia, or in an alcoholic solution of silver nitrate. Treatment with the latter solution also increases the sensitiveness of a silver bromide gelatin plate which has been coloured with eosin.

The gelatin can be completely removed from silver bromide in the ordinary emulsion by prolonged washing; some of the colouring matter in the coloured plates also remains firmly combined with the gelatin or silver bromide. The maximum of sensitiveness in the silver bromide gelatin plates coloured with eosin or aniline-red does not correspond with the maximum of absorption of the coloured gelatin. The former maximum lies nearer the red end of the spectrum than the latter.

The author is of opinion that the silver bromide gelatin plates which have been sensitised with cyanin or iodine-green yield much better results than "collodion emulsion" in photographing the red end of the spectrum.

W. C. W.

**Oxidation of Ammonia in Spring Water.** By H. FLECK (*Chem. Centr.*, 1884, 676—677).—W. Hempel has shown that the presence of calcium hydrogen carbonate in water essentially favours the formation of nitrate, whilst the presence of other calcium salts, for example, the sulphate, does not facilitate it. The author has ascertained that this oxidation, usually ascribed to the action of organised forms, can proceed without those forms. He employs two beakers placed at different levels, and connected by a fold of filter-paper. A liquid passing from the upper glass to the lower one by means of the paper is largely exposed to the air. Ammonia water thus treated gives rise to the formation of ammonium nitrite. Ammonia above a certain amount stops the oxidation. A 1 per cent. solution is ineffective, whilst a 0.2 per cent. solution shows the nitrite reaction with iodide-zinc-starch solution very clearly. With 0.1 per cent. the water in the lower beaker has a neutral reaction, and gives the nitrite reaction; it contains ammonium nitrate along with the nitrite. Presence of calcium hydrogen carbonate, as well as sterilisation of the paper by mercuric chloride, or by exposure to a temperature of 140°, does not prevent oxidation. It may readily be understood that in a porous soil, such that the enclosed gases are readily changed, and water with much less than 1 per cent. of ammonia is present, the formation of nitrate and nitrite can proceed without the intervention of organised forms.

J. T.

**Potassium Dichromate as an Antiseptic.** By LAUJORROIS (*Chem. Centr.*, 1884, 676).—Potassium dichromate (1 per cent.) acts as an antiseptic, preventing the putrefaction of urine and milk. Three eggs were taken, of which one was left whole, the second was

injected with 10 drops of a 1 per cent. solution of dichromate, and the third was injected with 10 drops of a 1 per cent. carbolic acid solution. After three months the first and second were undecomposed, whilst the third was quite rotten. Dichromate cannot be used for food preservation on account of its poisonous properties.

J. T.

**Water-vapour in Gas Generators.** By A. SCHMIDT (*Chem. Centr.*, 1884, 203—205).—The author considers the effect of working with and without the introduction of steam when coke is the fuel employed in the generator.

*Coke-gas without Steam.*—From calculations given, a unit-weight of carbon burnt to carbonic oxide develops 2480 heat-units in the generator, and the gas produced has a calorific value of 826; consequently an excess of heat is produced there which more than compensates for the loss by radiation.

*Coke-gas with Steam.*—The gas produced has a calorific value of 1772, which is more than double that produced without steam. In practice, however, the gas formed would be less favourable, as the heat lost by radiation must be produced by the combustion of more carbon by the air.

*Theoretical Maximum of Steam.*—Theoretically a coke with 10 per cent. ash, 5 of moisture, and 85 of carbon, would require 60 per cent. of steam to obtain the best results. But in practice the maximum can never be reached.

*Economy of Fuel.*—With 18 kilos. of steam, there is produced as above 54 kilos. of carbonic oxide with 23·14 kilos. of carbon. If this amount of carbon be burnt without steam, 54 kilos. of carbonic oxide and 103 kilos. nitrogen, together 157 kilos. of gas, whose calorific value is 826, are formed, so that the gas could produce  $157 \times 826 = 129,682$  heat-units. If the same amount of carbon be burnt with steam, then, as is shown in the paper, 54 kilos. carbonic oxide, 2 kilos. hydrogen, and 50 kilos. nitrogen, total 106 kilos. of gas, would be produced, whose calorific value is 1770; the total heat producible by this gas would be  $106 \times 1770 = 187,620$  units. Hence the gain with steam amounts to  $187,620 - 129,682 = 57,938$ , roundly 58,000 units of heat. To produce this amount of heat  $58,000 \div 8080 = 7\cdot17$  kilos. of carbon would be required, or  $23\cdot14 + 7\cdot17 = 30\cdot31$  kilos. Hence the economy in fuel amounts to 23·6 per cent. This gain is evidently not an absolute one, as all the heat set free in the generator is not lost. For large works with a central arrangement of generators the gain by the use of steam would be considerable, but with a separate generator for each furnace, and the two in close proximity, the gain is not so great. In both cases, however, the admission of steam acts beneficially in utilising heat produced in the generator, so that the walls are protected, and less sintering of the ashes takes place.

J. T.

**Obtaining Hydrochloric Acid from Calcium Chloride.** By E. SOLVAY (*Dingl. polyt. J.*, 255, 307).—The author has found that by mixing calcium chloride with silica and alumina in such proportions that the calcium chloride present in the mixture corresponds with the theoretical quantity of silica and alumina, a mass is obtained which

fuses at the temperature at which the reaction takes place, so that the working of the apparatus is greatly hindered. On adding more silica and alumina the product is rendered more infusible, but loses the property of forming a good cement. The residue is no longer basic, and not clean enough. It is possible to overcome these difficulties by adding to the mixture a sufficient quantity of residue from a preceding treatment. The new mixture is found to resist the action of heat, although it contains as much lime as that prepared with the theoretical quantity of calcium chloride, silica, and alumina. D. B.

**Obtaining Iodine in Peru.** (*Dingl. polyt. J.*, 255, 299.)—According to the *Génie civil*, 1884, 5, 106, about 1600 kilos. of iodine are produced monthly at the works of Peruana in the province Tarapaca, in Peru, from the iodous mother-liquors obtained in the manufacture of sodium nitrate. The forms of apparatus constructed by R. Harvey and J. T. North in 1881 are employed for the preparation of the hydrogen sodium sulphite used to precipitate the iodine, and for distilling the latter. The hydrogen sodium sulphite is obtained by saturating a solution of soda with sulphurous anhydride. The soda is prepared by furnacing an intimate mixture of sodium nitrate and coal-dust. The essential constituent of the product of the reaction is soda contaminated with sodium chloride, sodium sulphate, earthy ingredients, and unburnt coal. D. B.

**Composition of the Gas from Pyrites Burners, and the Influence of the Glover Tower in the Manufacture of Sulphuric Acid.** By SCHEURER-KESTNER (*Compt. rend.*, 100, 636—638).—Sulphuric anhydride is rarely absent from the gas from pyrites burners (see this vol., p. 199), and it sometimes amounts to as much as 9 per cent. of the total quantity of sulphurous anhydride produced. The sulphuric anhydride is rapidly converted into sulphuric acid by the moisture in the air, and no anhydride is found in the gas after it has passed through the flue connecting the burners with the condensing apparatus. The acid which is thus formed is condensed in the Glover tower.

During 16 days, the acid introduced into the Glover tower and that running from it was collected, and it was found that 15·7 per cent. of the total acid produced was formed in the Glover tower. In another experiment the acid formed in the chambers was collected separately, and the proportion formed in the tower was found to be 16·3 per cent. of the total yield. This proportion represents almost exactly the increase in the producing power of the chambers resulting from the use of the Glover tower; at Thann this increase is 15—18 per cent.

The formation of sulphuric acid in the Glover tower is due (1) to the condensation of the sulphuric acid formed by the hydration of the sulphuric anhydride in the burner gases; (2) to the action of the sulphurous anhydride on the nitrogen oxides from the nitrated vitriol; (3) to the occurrence in the upper part of the tower of the same reaction or reactions that take place in the leaden chambers.

C. H. B.

**Method of Hardening Plaster.** By JULIE (*Compt. rend.*, 100, 797—799).—Plaster is the only material for building purposes which increases its volume after application, but it possesses the disadvantages of want of firmness. It is proposed to harden it by mixing 6 parts of plaster with 1 part of rich lime, drying the mixture, and then soaking it for a short time in the sulphates of metals precipitated by lime, of which the most convenient are those of zinc and iron. If the latter be used the plaster assumes after a time the characteristic tint of ferric oxide, but its resistance to fracture is 20 times as great as ordinary plaster. Such a mixture may also be used as a cheap substitute for parquetterie flooring. V. H. V.

**Improvements in Metallurgy.** (*Dingl. polyt. J.*, 255, 375—388 and 421—426.)—To increase the durability of basic linings, W. F. Batho proposes to mix the composition forming the lining with 10 per cent. of iron or steel wire cuttings.

P. Lambertz has patented an arrangement for producing acid or basic ingot steel, cast steel, or refined pig-iron, in a Bessemer converter (Ger. Pat., 29,571, April 1884). To arrange the manufacture of iron so that it may be produced either by the blast-furnace process or hearth smelting process, T. Williamson recommends that a Bessemer converter should be connected with Siemens' heating chambers.

The working of the Bessemer and Thomas processes in small converters is discussed by A. Trappen (*Stahl und Eisen*, 1884, 524), W. Hupfeld (*Oester. Zeit. Berg. und Hütt.*, 1885, 1), and P. v. Turner (*ibid.*, 1885, 41).

To lessen the friction of the air passing through the converter tuyeres, C. Thompson proposes to enlarge the passages of the tuyeres towards the back end.

C. A. Caspersson has patented an arrangement whereby the gases contained in ingots can escape during the process of casting. For this purpose, the funnels are provided with a perforated sieve-like bottom. (Ger. Pat., 29,585, March 1884.) With the same object in view, H. A. Brustlein proposes to pour the ingots into moulds, the bottom of which consists of metal, preferably copper, cooled by a continuous stream of water. D. B.

**Volatilisation of Zinc from German Silver Alloys.** By A. R. HASLAM (*Chem. News*, 51, 123—124).—2.258 grams of each of the following alloys was heated to bright redness in a porcelain crucible in a current of dry hydrogen, and weighed every hour. The alloys had the composition: I, Cu 53.5, Ni 14.3, Zn 31.8, Fe trace; II, Cu 50.4, Ni 17.6, Zn 31.2; III, Cu 56.3, Ni 11.4, Zn 31.9; the loss per hour in grams was as follows:—

	1st hour.	2nd.	3rd.	4th.	5th.	6th.	Total loss.
I.	0.056	0.052	0.045	0.038	0.026	0.016	0.233
II.	0.050	0.044	0.034	0.024	0.016	0.014	0.182
III.	0.058	0.056	0.050	0.044	0.037	0.029	0.274

The more nickel the alloy contains, the greater is the difficulty of dis-

sociating it. The correctness of this inference is supported by further experiments; for example, a sample of brass containing 30.6 per cent. of zinc lost 0.424 gram in six hours, and when heated more strongly retained from 0.6 to 1 per cent. of zinc; whereas an alloy approximately of the formula  $\text{NiZn}_2$  lost 0.122 gram in six hours, and in the subsequent heating retained 9 per cent. of zinc. D. A. L.

**Reynolds' Process for Parting Gold from Bars.** By F. GUTZKOW (*Dingl. polyt. J.*, **255**, 303).—It is stated that in separating gold and silver, the latter is dissolved more readily when in the form of bars than when in a granulated condition, a circumstance on which Reynolds' process for parting gold from silver by means of sulphuric acid depends. D. B.

**Distillation of American Petroleum.** By D. MENDELÉEFF (*Bull. Soc. Chim.*, **43**, 109–110).—On carefully fractioning the portion of Baku (Caucasian) petroleum which boils between  $50^\circ$  and  $120^\circ$ , the density of the fractions diminishes as the boiling point rises from  $55\text{--}62^\circ$ , from  $80\text{--}90^\circ$ , and from  $105\text{--}110^\circ$ . American petroleum shows the same peculiarity; thus the sp. gr. of the fraction boiling at  $80^\circ$  is 0.7347 at  $17^\circ$ , which is the same as the sp. gr. of the fraction boiling at  $75^\circ$ ; beyond this point the gravity augments as the temperature is raised until  $104^\circ$ , when the sp. gr. is 0.7543 at  $17^\circ$ , and again diminishes, being 0.7270 at  $17^\circ$  for the fraction between  $115^\circ$  and  $117^\circ$ , the same density as those boiling at  $98^\circ$  and at  $85^\circ$ . The gravity then again augments with the temperature from  $117\text{--}125^\circ$ . American and Caucasian petroleum are therefore similar in this respect, but the densities of fractions boiling at equal temperatures are different, thus the gravity of that fraction of Baku petroleum boiling at  $80^\circ$  is 0.7486 at  $17^\circ$ , whilst that of American coming over at the same temperature is 0.7347 at  $17^\circ$ . The relative quantities of the fractions are also different for the two petroleum. A. P.

**Fusel Oil in Spirit.** By G. LUNGE, V. MEYER, and E. SCHULZE (*Chem. Centr.*, 1884, 854–858).—*Technical Purification of Spirit.*—In order to remove fusel oil, which consists essentially of higher homologues of ethyl alcohol, treatment with wood-charcoal, in combination with thorough rectification, gives the best results. The purest form of ethyl alcohol, produced technically, is thus obtained, which when taken in a diluted state does not show the poisonous action of fusel oil. Pictet's method of fractional distillation under reduced pressure, and Naudin and Schneider's treatment of potato spirit with coppered zinc, give scarcely better results. In all cases where it is only required to detect fusel oil, the qualitative method given by Otto can be applied, provided that no ethereal oils are present; the method is easily and quickly applied. If, however, the amount of fusel oil be small, the method is not good, whilst by Marquardt's method even traces of fusel oil can be detected. The latter is the more sensitive, as there is no risk of loss by volatilisation, and as the odour of valeric acid is much more characteristic than that of fusel oil. All other methods have little or no value; no easy process

is known for methods of estimating the amyl alcohol in brandy. Experiments were made with B. Röse's method, but the results so far obtained cannot be considered as a solution of the problem, since in practice the sample contains many unknown substances. Röse's method is based on the more ready solubility of the higher alcohols in chloroform than in 50 per cent. alcohol. J. T.

**Sulphurous Anhydride in Sugar Refining.** By L. BATTUT (*Chem. Centr.*, 1884, 854).—As refining agent 1 per cent. of a solution of 8—10 per cent. strength is added to the crude juice. The insoluble substances produced are filtered off. In decolorising, the gas is used. When employed in the first case, it is possible to diminish the amount of lime used without reducing the purity of the product. The acid only produces glucose in beet-juice after long exposure to the air. J. T.

**Recovery of Beet-juice by Lime, &c.** By A. FROMENTIN and MANOURY (*Bied. Centr.*, 1885, 128—129).—Fromentin, to prevent decomposition of the sections in the diffusion apparatus, adds 8—10 litres of milk of lime (30° B.); this allows of more juice being expressed, but its quality is inferior; if only 2—3 litres (25° B.) are added, the quality is not injured. The purity of the diffusion liquid before addition of lime was 75—76, afterwards it was 77—78; this process appears to improve the appearance of the mark, which was quite white and hard, and kept well, and was as palatable to cattle as the other produced without lime. To purify the juice in the cells before expression, and to render the albuminoids insoluble within the cells, Manoury adds 0.3—0.5 per cent. of lime, and heats for a short time at 85—90°, after which the juice can readily be expressed. He has also employed ferric chloride and a mixture of lime with zinc chloride. E. W. P.

**Preparation of Salicylic Acid.** By R. SCHMITT (*Dingl. polyt. J.*, 255, 259).—On saturating the dry phenates of the alkalis and alkaline earths with dry carbonic anhydride at the ordinary temperature, the alkali salts of the phenyl carbonates are formed in quantitative proportions, for instance, phenyl sodium carbonate is obtained from sodium phenate, thus:  $C_6H_5 \cdot ONa + CO_2 = C_6H_5O \cdot COONa$ . On heating these salts in high pressure cylinders at 120—140° intermolecular conversion into the normal salicylate is effected, phenyl sodium carbonate being transformed into sodium salicylate, thus:  $C_6H_5O \cdot COONa = HO \cdot C_6H_4 \cdot COONa$ . The resulting salicylate is dissolved in water, the salicylic acid precipitated by a mineral acid and purified by crystallisation.

According to another method, the phenates of the alkalis or alkaline earths are dried thoroughly and put into a boiler, into which dry carbonic anhydride is pumped until the formation of the phenyl carbonate has been completed. The boiler is then closed, and after standing for some hours is heated in an air-bath at 120°—140° to effect the conversion into the normal salicylate.

The dry phenates may also be filled into a boiler with enough car-



bonic anhydride to form phenyl carbonate, after which the boiler is closed, and the process continued in the above described manner.

D. B.

**Bleaching Tallow.** (*Chem. Centr.*, 1884, 912).—The tallow is partly saponified by heating with caustic soda solution and salt, and the upper and lower saponified layers used for the preparation of curd-soap. The middle unsaponified layer is filtered through linen, heated to boiling with a  $2\frac{1}{2}$ –3 per cent. aqueous solution of alum for about 15 minutes, and then allowed to stand for 3 to 5 hours. It is then again heated to a temperature of 170–200°, when it becomes snow-white. The heating must be stopped the moment any unpleasant smell is detected (even if the temperature has not reached 170°), as otherwise it again becomes discoloured. Rancid fat cannot be employed in this process, but the fat should not be too fresh, as then the saponification is often very rapid.

L. T. T.

**Tengkawang Fat or Vegetable Tallow.** By H. P. BAKKER (*Pharm. J. Trans.* [5], 15, 407–409 and 428–430).—In this paper, an account is given of the planting and growth of the trees, and of the character and mode of treatment of the fruit yielding the tengkawang fat. The trees are six in number and are called *Tengkawang toengkoel*, *T. rambei*, *T. eajar*, *T. goentjang*, *Madjan*, and *Terindak*. When the fruit (a nut) falls off, it is gathered, steeped in water for 30 days, and the pulp is then air-dried, or the fruit is dried directly, the fat is extracted from the dry material by simultaneous steaming and pressing. The soaking in water increases the yield of tallow and prevents the fruit when stored being attacked by worms. Germination of the seeds lowers the yield of fat.

D. A. L.

**Preparation and Utilisation of Grape-seed Oil.** By J. v. JOBST (*Dingl. polyt. J.*, 255, 450).—The extraction of oil from grape stones being very imperfect when pressure was used, the author treated the carefully-dried and crushed stones with carbon bisulphide, and obtained about 10 per cent. of a thick green oil. This was purified by several filtrations through charcoal, and gave an oil having a pale straw-colour and disagreeable taste and odour. The oil has a sp. gr. of 0.926 at 17.5°, dissolves readily in ether, is sparingly soluble in alcohol, and is hydrolysed by treatment with an alcoholic solution of potash. It solidifies at –11° and may be used for illuminating purposes, or preferably for soap-making.

D. B.

**Synthesis of Dyes on Tissues.** By L. MARGARY (*Gazzetta*, 14, 268–270).—By the action of methyl iodide or nitrate, or of ethyl iodide, rosaniline yields methyl- and ethyl-derivatives: similarly by the action of aniline in the presence of benzoic or salicylic acids, phenyl-derivatives are formed. It is shown in this paper that these transformations can be effected directly on tissues. For example, if cotton mordanted and dyed with magenta be heated with methyl iodide in methyl alcohol in a sealed tube the rose colour will pass into a violet; on the addition of more methyl iodide, the violet is changed to the iodine-green. The converse changes can be effected by warming

the cotton, when the methyl-derivatives are dissociated into magenta and methyl iodide. By this means, iodine-green can be distinguished from malachite-green, which is unaltered by heating. Similarly it is shown that the azure-blue of triphenylrosaniline can be synthesised on tissues by heating the material dyed with magenta with aniline and a trace of benzoic acid.

Ferric salts are suggested as a useful test for distinguishing the various blue dyes when fixed on tissues, thus induline-blue is converted by it into a greyish-black colour; whilst the aniline-, diphenylamine-, and methylene-blues are unaltered, and indigo-blue is oxidised and decolorised.

V. H. V.

**Preparation of Violet Colouring Matters.** (*Dingl. polyt. J.*, 255, 260.)—The *Badische Anilin und Sodafabrik in Ludwigshafen* has patented a process for preparing methyl-violet, which consists in passing from 18 to 20 kilos. carbonyl chloride into 100 kilos. of dimethylaniline at 20°, and adding, after the lapse of 24 hours, 50 kilos. dimethylaniline and 30 kilos. of powdered zinc chloride. The mixture is then agitated, and carbonyl chloride passed in at 40° to 50°, until the weight has been increased by 20 kilos. After six hours' heating at 50°, the reaction is completed. The colour base is separated from the melt thus obtained by saturation with soda-ley, and distillation by means of steam. It is converted into the sulphate, and the hot solution of the latter treated with salt, when the hydrochloride of methyl-violet crystallises out.

For the preparation of violet dyes from diethylamine and methylethylaniline the same method is adopted.

D. B.

**Vinicolore.** By JAY (*Bull. Soc. Chim.*, 42, 217—218.)—This is sold in France as an artificial colouring agent for wine. It consists of elderberries mixed with Biebrich-red.

W. R. D.

**Dyeing with Alizarin on Indigo.** By A. SCHEURER (*Dingl. polyt. J.*, 255, 452).—A mixture of aluminium chloride and potassium dichromate, thickened with starch, is printed on indigo-blue cloth. The latter is then steamed for one minute in Mather and Platt's apparatus, washed, dyed with alizarin, and soaped.

D. B.

**Preparation of Wood Stains in the Solid Form.** By L. E. ANDÉS (*Chem. Centr.*, 1884, 37, 702—703).—*Oak stain*.—5 grams of Cassel-brown is boiled with 0.5 kilo. potash, and 10 grams rain-water, for one hour. The resulting dark liquid is strained through linen, boiled to a syrupy consistency, and poured into sheet-iron pans; when set, it is pressed, and then ground to a rough powder. The other stains are obtained in the solid form by similar procedure.

*Light oak stain*.—3 kilos. of catechu are boiled with 7 of rain-water, filtered hot through linen, evaporated to a syrupy consistency, and a solution of 250 grams potassium dichromate in 2 kilos. water added.

*Walnut stain*.—3 grams of Cassel-brown are boiled with 0.3 gram potash and 7 grams of water. The extract strained through linen and evaporated with 2.5 grams of logwood extract.

*Rosewood stain.*—1 kilo. Cassel-brown, 0.10 kilo. potash, and 3 kilos. water, are boiled, and the solution strained; 4 grams Brazil-wood extract dissolved in boiling water is then added.

*Mahogany stain.*—3 kilos. Brazil-wood extract, 0.25 kilo. potash, and 3 kilos. water are boiled together; 150 grams of eosin added, and the liquid evaporated to a syrupy consistency.

*Palisander stain.*—Prepared like mahogany, using 200 grams magenta and 25 grams aniline-blue in place of eosin.

*Satin-wood stain.*—3 kilos. fustic is boiled with 7 kilos. of water, strained, and evaporated to a syrup; a solution of 100 grams of potash in 350 of water is added, and the whole evaporated to dryness.

*Ebony stain.*—5 kilos. logwood extract, boiled with 11 kilos. water, strained, and evaporated to a syrup, 300 grams of ferric nitrate added, and the mass well stirred.

H. P. W.

**A Substitute for Caoutchouc.** By G. HAUG and C. HOFFMANN (*Dingl. polyt. J.*, **255**, 215).—The skins of hares, rabbits, and other small animals, are washed in water, unhaired by steeping in lime-water, and boiled with 5 per cent. of crude glycerol and a small amount of water in a Papin's digester until the mass has been completely dissolved. A thick and tough substance is obtained, which is dried on nets in a current of air, or treated in the following manner. 12 parts are melted with 12 parts of crude glycerol in a steam-bath, and treated with 1 part of a concentrated solution of potassium dichromate. The liquid mass thus formed is poured into moulds, and allowed to solidify under pressure. The moulded mass is then dried in a dark room. It resembles vulcanised caoutchouc, and is said to resist the action of heat better than the latter.

D. B.

**Bismuth and Pepsin.** By R. ROTHER (*Pharm. J. Trans.* [3], **15**, 144).—When 1 part of bismuth citrate is heated with 2 parts of ammonium, sodium, or potassium hydrogen carbonate, or with 1 part of sodium or potassium carbonate, and sufficient water, carbonic anhydride is evolved and complete solution takes place. The compound formed with potassium hydrogen carbonate is freely soluble. It has an acid reaction, but does not precipitate pepsin. It is therefore recommended for use in the preparation of a permanent acidulous solution of bismuth and pepsin, for which purpose a formula is given in the paper.

D. A. L.

**Kola Nuts, *Sterculia Acuminata*.** By NATTON (*J. Pharm.* [5], **10**, 257—259).—The nut possesses tonic, nutritive, exciting, and aphrodisiacal properties. It is employed either fresh or roasted. It contains much caffeine, some theobromine and tannin; and it being thus astringent and tonic is recommended for chronic diarrhoea, cardiacal affections, and for cachexy. A number of receipts are given.

H. B.

## General and Physical Chemistry.

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**Spectrum of Ozone, and the Presence of Ozone in the Atmosphere.** By E. SCHOENE (*Jour. Russ. Chem. Soc.*, 1884 [2], 250—252).—The absorption-spectrum of ozone was examined, and found to be well in accordance with the description given by Chappuis. Besides the 11 bands observed by this investigator, one more was detected at wave-length 516, and another, still subject to some doubt, at about 452. The quantity of ozone in a gas may be determined with the spectroscope; since for a source of light of given intensity, the increase in the amount of ozone is accompanied by the successive appearance of the absorption-bands, the principal band (between 595 and 613) appearing first, the rest following in the order of their intensity.

The spectrum of the atmosphere was examined for some time daily before sunrise and after sunset when the rays passed through a thick layer of air, the remarkable crepuscular phenomena observed throughout the whole of the globe at the end of 1883 having proved highly favourable to these investigations. Although the band of water (599—610, in the liquid, not in the solid state) coincides partly with the main band of ozone, observations made in intense frost, and the sky being entirely bright, leave scarcely any doubt whatever as to the presence of ozone in the atmosphere. The bands are not distinctly seen when the spectroscope is directed towards the sun itself. Another cause interfering with this kind of observation is due to the so-called rain-band (partly coinciding with the main ozone-band, and extending to line D), which became so intense in spring that it was difficult to detect the presence of ozone in the air. The latter is probably also the reason why in climates more warm and damp than that of Central Russia, the ozone-band could not be observed in the absorption-spectrum of the atmosphere. A. T.

**Relation between the Ultra-violet Spectrum of Water-vapour and the Telluric Bands A, B,  $\alpha$  in the Solar Spectrum.** By H. DESLANDRES (*Compt. rend.*, 100, 854—857).—The ultra-violet region of the emission spectrum of the vapour of water contains three bands which terminate abruptly on the most refrangible side, but fade gradually away towards the red. The first is an intense band at 306.2 (Huggins), the second, weaker, at 280.5 (Liveing and Dewar), and the third, very feeble, discovered by the author, at 261.05. The three bands resemble in appearance the three telluric bands A, B,  $\alpha$  in the solar spectrum, which according to Egoroff are due to oxygen alone.

The author has produced the spectrum of pure water-vapour under low pressure in Piazz-Smyth and Monckhoven spectrum tubes; under low pressure in presence of excess of hydrogen or oxygen; by combustion, and under various other conditions. He finds that the bands

A, B,  $\alpha$  in the spectrum of water-vapour are geometrically similar to the telluric bands, and include all the rays observed in the latter, with the same relative intensities and distances, but they are much larger, and the bands A and B include a second series of rays of the same type, but more refrangible and weaker. C. H. B.

**Chemical and Physiological Action of Light on Chlorophyll.**

By C. TIMIRIAZEFF (*Compt. rend.*, 100, 851—854).—In order to avoid errors due to the unequal dispersion of a prism, the author has adopted the method of decomposing portions of the previously dispersed light.\* By means of the cylindrical lens and prism of small angle used in experiments on complementary colours, two images, complementary in colour, were thrown at the same time either on two *eprouvettes* containing a 30 per cent. solution of carbonic anhydride in which was placed a small branch of *ellodea*, or on a plate coated with collodion containing a small quantity of chlorophyll. When the spectrum was divided into two equal parts with respect to the normal spectrum, the two images were of course respectively yellow and blue. The maximum chemical and physiological effect was exerted by the yellow, whilst the effect of the blue rays was scarcely appreciable. The blue-violet portion of the spectrum being cut off by a screen, the less refrangible portion was divided into two equal parts, red and greenish-yellow. The maximum chemical and physiological effect was exerted by the red. By placing the prism in the greenish-yellow part of the spectrum, a greenish-yellow and a violet image were obtained. The latter contained all the rays absorbed by chlorophyll, whilst the former contained only the green, which is reflected by vegetation. In this case the maximum effects were exerted by the violet.

It follows from these results that chlorophyll acts as a true sensitizer, undergoing decomposition itself, and promoting the decomposition of carbonic anhydride in those parts of the spectrum which it absorbs. The different rays absorbed by chlorophyll produce decomposition in very different degrees, the maximum decomposition coinciding in a remarkable manner with the maximum energy in the normal spectrum as measured by Langley and Abney. It would seem, therefore, that it is the amplitude rather than the period of the vibrations which brings about that disturbance of the carbonic anhydride molecule which finally results in its dissociation. The chemical action of light on the photographic plate seems to be strictly analogous to its physiological action on the living plant, provided that, as in the case of chlorophyll, the absorption phenomena are identical in both cases. C. H. B.

**Battery with a Circulating Liquid.** By J. CARPENTIER (*Compt. rend.*, 100, 849—851).—The essential part of this battery is a syphon with unequal limbs, both of which are plunged in the same vessel containing the exciting solution. In the longer limb are placed

\* The author ascribes this device to Paul Bert (*Compt. rend.*, 1878), but it was employed many years ago by J. W. Draper (see *Phil. Mag.*, 1872, and "Draper's Memoirs").—C. H. B.

the electrodes, consisting respectively of zinc and carbon, and the syphon is filled in any convenient way. So long as the circuit remains open the liquid in the syphon remains homogeneous, and equilibrium is maintained, but as soon as the circuit is closed the zinc dissolves and increases the density of the liquid in which it is immersed. Hydrostatic equilibrium is thus disturbed, and a circulation of the liquid is established proportional to the intensity of the current. The heavy liquid containing the zinc falls to the bottom of the vessel and remains sharply separated from the fresh solution, whilst the latter continually ascends the short limb of the syphon and is brought in contact with the electrodes.

In the cell constructed by the author, the carbon electrode constitutes one limb of the syphon, and is in the form of a tube, in the centre of which is suspended the amalgamated zinc. The other limb consists of the annular space between the carbon tube and the surrounding glass envelope, communication between the two being established by means of a ring of holes pierced in the upper part of the carbon. The position of the electrodes is so arranged that the level of the exciting liquid is somewhat higher than the ring of holes. Several elements of this form may be placed in one and the same reservoir, if care be taken to isolate them sufficiently from one another by means of glass or caoutchouc envelopes with small apertures at top and bottom.

C. H. B.

**New Apparatus for Electrolysis.** By M. ROSENFELD (*Ber.*, 18, 867—869).—A description of an apparatus for demonstrating the composition of hydrochloric acid by electrolytic decomposition.

P. P. B.

**Production of Low Temperatures by means of Liquid Oxygen, Nitrogen, Carbon Monoxide, and Atmospheric Air.** By S. v. WROBLEWSKI (*Monatsh. Chem.*, 6, 204—248).—The author describes the form of apparatus he employs for the liquefaction of oxygen, nitrogen, &c. The refrigerant used is liquid ethylene, by means of which a temperature of  $-152^{\circ}$  can be obtained. The low temperatures are measured by the aid of a galvanometer and a thermoelectric couple of copper and German silver. Under the ordinary atmospheric pressure oxygen boils at  $-181.5$ , and nitrogen at  $-193.2^{\circ}$ . The vapour-tension of liquid nitrogen is 32 atmospheres at  $-146^{\circ}$ . Carbon monoxide boils at  $-190^{\circ}$  under the atmospheric pressure.

The critical pressure of oxygen is about 50 atmospheres, and the critical temperature about  $-118^{\circ}$ .

Liquid atmospheric air boils between  $-187^{\circ}$  and  $-191.4^{\circ}$  under a pressure of 740 mm., but the liquid loses nitrogen on boiling, and its boiling point gradually sinks. Under a pressure of 20 mm., oxygen boils at  $-200.4^{\circ}$ . Nitrogen boils at  $-203^{\circ}$  under a pressure of 65 mm., and solidifies to a crystalline mass.

Carbon monoxide easily solidifies at  $-199^{\circ}$ . The tension of its vapour at this temperature is equal to 100 mm. As the readings of the hydrogen thermometer cease to agree with the results calculated

by the aid of the galvanometer at this temperature, it is probable that hydrogen approaches its point of liquefaction at  $-200^{\circ}$ .

W. C. W.

**Heats of Formation of Hydrogen Compounds.** By D. TOMASSI (*Bull. Soc. Chim.*, **43**, 221—22.)—The heats of formation of most of the combinations of the acid radicles with hydrogen as obtained by experiment, agree very closely with those calculated from the thermic constants of the components. Hydrogen cyanide, however, shows a considerable discrepancy, which is probably due to the dissociation of the aqueous solution of potassium cyanide with which the experimental determination is made. Mercury cyanide undergoes but slight dissociation on dissolution in water, and from this salt the heat of formation of hydrogen cyanide may be calculated by a method detailed in the paper. In this way it is found that its apparent deviation from the law is due to dissociation, and also that its coefficient of dissociation determined by a simple calculation from this deviation agrees very closely, in fact is almost identical with the coefficient calculated on the ground of the difference between the theoretical and practical vapour-density of solutions of hydrogen cyanide in water.

A. P.

**Heats of Formation of some Salts of the Amines in Dilute Solutions.** By A. MÜLLER (*Bull. Soc. Chim.*, **43**, 213—217).—The following table gives the results of the determinations of the heats of formation of the chlorides, carbonates, and hydrogen carbonates of ammonia, amylamine, and mono-, di-, and tri-ethylamine. The method of determination used was checked by comparison with the results obtained by Berthelot for the heats of combination of ammonium chloride and trimethylamine hydrochloride.

	$2(\text{NR}_3\text{HCl})$ .	$(\text{NR}_3)_2\text{CO}_3\text{H}_2$ .	$(\text{NR}_3)_2\text{CO}_3\text{H}_2$ .
Ammonia . . . . .	24.9 cal.	12.3 cal.	19.4 cal.
Monomethylamine.	26.1 „	16.0 „	18.0 „
Dimethylamine . .	23.2 „	12.6 „	15.8 „
Trimethylamine . .	17.5 „	8.3 „	9.7 „
Amylamine . . . . .	27.4 „	16.4 „	19.4 „

The coefficients of dissociation of the hydrochlorides of these amines rise with the temperatures of formation, as may be experimentally shown by making molecular solutions in equal volumes of water, and adding to each solution a drop of alkaline litmus solution. If the solutions thus prepared be left under a bell-jar over sulphuric acid, they after a few days gradually show an acid reaction, and in the following order:—Trimethylamine, ammonia, dimethylamine, monethylamine, and amylamine.

A. P.

**Fractional Distillation in a Current of Steam.** By M. J. LAZARUS (*Ber.*, **18**, 577—579).—Naumann has shown that when a non-miscible liquid is distilled in a current of steam, it passes over below  $100^{\circ}$ . The author finds that this may be taken advantage of in separating mixtures of substances not miscible with water and whose boiling points lie some distance apart. When distilled in a current of steam

the substance of lowest boiling point passes over first. Various mixtures were successfully separated in this way. This method is especially useful in separating mixtures where one of the constituents is easily decomposable, and ordinary fractional distillation cannot therefore be resorted to.

L. T. T.

**Kahlbaum's so-called "Specific Remission" as an Expression of the Dependence of the Boiling Point on Atmospheric Pressure.** By A. NAUMANN (*Ber.*, 18, 973—976).

**Specific Volumes of Chlorine, Bromine, and Iodine in Carbon Compounds.** By M. SHALFÉEFF (*Jour. Russ. Chem. Soc.*, 1884 [i], 679—687).—Tables are given containing the calculated numbers for the specific volumes of the halogens in their different organic compounds. The following are the results deduced:—

1. That the volumes of the halogens in these compounds are multiples of three.

2. That the halogens on entering into combination exhibit a faculty of condensation which is in inverse relation to their atomic weight; thus bromine enters into some, iodine into all of its compounds with an increased volume. The numbers deduced from the three elements in organic compounds approximate for chlorine to 21 (in most organic compounds considerably inferior to this number, but approaching to it the nearer the greater the number of chlorine-atoms in the molecule of the compound), to 24 in chloranhydrides, the specific volume of the element in the free state being 27; for bromine it is 24 in most of the carbon compounds, 27 in the free state, and probably 30 in bromanhydrides; for iodine 27 in carbon compounds, and 26 in the free state.

A. T.

**Constants of Capillarity of Liquids.** By R. SCHIFF (*Gazzetta*, 14, 368—447).—In a former memoir (*Abstr.*, 1884, 808) on the constants of capillarity of liquids at their boiling points, the author pointed to the advisability of tracing out the relationship between the relative number of molecules of different liquids elevated along the line of contact between the liquid and solid surfaces. This constant

is  $N = \frac{\frac{1}{2}a^2d}{m} = \frac{a^2}{2v}$ ; for convenience the values for  $N 10^3$  are used. It

was further established that the constant depends upon the number and arrangement of the atoms within the molecules; as regards the former, the atoms of carbon, oxygen and chlorine can be considered equivalent to 2, 3, and 7 atoms of hydrogen respectively, or the constant can be deduced from a logarithmic curve of the form  $N = \frac{e^{(a-b)H}}{H}$ , in

which  $e$  is the base of natural logarithms and  $a$  and  $b$  are constants, namely, 6.48293 and 0.016763. As regards the arrangement of the atoms, the exceptions of diallyl and ethylene chloride to the otherwise general concordance between the calculated and experimentally determined values for  $N$  seemed to indicate that this constant varies according to the nature of the atomic concatenation.

In this paper the latter point is more particularly discussed, and



numerous determinations are given of the capillary constants of liquids belonging to various series of chemical types. Although in the previous experiments the boiling point was selected as the point of most approximate physical comparability, yet as in many cases liquids undergo either partial decomposition with evolution of gases, or change of molecular aggregation, or are affected by the carbonic anhydride and moisture of the atmosphere, it was found advisable to modify the simple form of apparatus so as to obtain a partial vacuum. Thus each limb of the U-tube was bent out, and the ends closed by stopcocks; between the bends there was a connecting tube also provided with a stopcock to equalise the pressure in both limbs. The observations of the capillary elevation were made with the tube previously exhausted, then closed; results obtained with the open and closed form are given by way of comparison. Further, in cases in which direct determinations of  $\alpha^2$  at the boiling point were unadvisable, a series of determinations were made at lower temperatures, and the values at the boiling point calculated by interpolation. The values for the specific volumes were taken from the researches of Kopp, Thorpe, Zander, the author, and others, and thus all the necessary quantities were obtained for the estimation of N in the above equation. In the table below are given the values for  $\alpha^2$ , either directly determined or calculated by interpolation of  $N 10^3$  and of T, the critical points calculated by dividing  $\alpha^2$  at the boiling point by the coefficient of depression and adding the number obtained to the boiling point.

Liquid.	$\alpha^2$ in mm.	$N = \frac{\alpha^2}{2v}$	T.	Molecular volume.
Terpene (from lemons), $C_{10}H_{16}$ . . . . .	3·772	10·1	366°	186·3
Formic acid, $H_2CO_2$ . . . . .	5·284	64·3	492	41·08
Acetic acid, $C_2H_4O_2$ . . . . .	3·872	30·6	375	—
Propionic acid, $C_3H_6O_2$ . . . . .	3·725	21·7	388	—
Butyric acid, $C_4H_8O_2$ . . . . .	3·545	16·4	395	—
Isobutyric acid, $C_4H_8O_2$ . . . . .	3·428	15·6	375	—
Valeric acid, $C_5H_{10}O_2$ . . . . .	3·283	12·6	392	—
Acetic anhydride, $C_4H_6O_3$ . . . . .	4·181	19·1	380	—
Methyl formate, $C_2H_4O_2$ . . . . .	4·944	39·6	—	—
Allyl acetate, $C_5H_8O_2$ . . . . .	4·106	16·9	—	—
Dimethyl acetal, $C_4H_{10}O_2$ . . . . .	4·303	19·4	261	—
Methyl amyl ether, $Me.O.C_5H_{11}$ . . . . .	4·085	13·8	281	148·13
Ethyl oxalate, $C_6H_{10}O_4$ . . . . .	3·562	10·7	422	—
Methyl benzoate, $C_8H_8O_2$ . . . . .	3·982	13·1	435	—
Ethyl benzoate, $C_9H_{10}O_2$ . . . . .	3·709	10·6	436	—
Ethyl acetoacetate, $C_6H_{10}O_3$ . . . . .	3·94	12·8	428	153·34
Anisoil, $C_7H_8O$ . . . . .	4·554	18·0	381	125·21
Phenetol, $C_8H_{10}O$ . . . . .	4·12	13·8	385	—
Methoxycresol, $C_8H_8Me.O.Me$ . . . . .	4·278	14·5	408	147·79
Dimethoxyresorcinol, $C_6H_4(OMe)_2$ . . . . .	4·097	13·0	454	137·13
Furfuraldehyde, $C_4H_3O.CO.H$ . . . . .	5·2	27·2	450	—
Valeraldehyde, $C_5H.O$ . . . . .	4·611	19·3	329	—
Cumaldehyde, $C_{10}H_{12}O$ . . . . .	3·83	10·2	494	—
Carvol, $C_{10}H_{14}O$ . . . . .	4·029	10·6	477	190·26
Pinacolin, $C_6H_{12}O$ . . . . .	4·267	15·4	312	138·25

Liquid.	$a^2$ in mm.	$N = \frac{a^2}{2v}$ .	T.	Molecular volume.
Isobutyl chloride, $C_4H_9Cl$ .....	4·127	18·1	—	114·26
Isoamyl chloride, $C_5H_{11}Cl$ .....	4·022	14·9	—	134·40
Chlorobenzene, $C_6H_5Cl$ .....	4·211	18·4	370°	—
Chlorotoluene, $C_6H_4MeCl$ .....	3·992	14·8	398	—
Benzyl chloride, $C_6H_5CH_2Cl$ ....	4·2	15·7	423	133·45
Propylene chloride, $C_3H_6Cl_2$ .....	3·881	18·6	—	107·59
Tetrachloroethylene, $C_2Cl_4$ .....	2·855	13·4	—	—
Trichlorethane, $C_2H_3Cl_3$ .....	3·159	16·8	—	—
Epichlorhydrin, $C_3H_5OCl$ .....	4·652	26·7	373	—
Chloral, $CCl_3CHO$ .....	3·021	14·1	327	—
Ethyl monochloracetate, $CH_2ClCO_2Et$ .....	3·529	14·4	—	—
Ethyl dichloracetate, $CHCl_2CO_2Et$ .	3·143	10·9	—	—
Ethyl trichloracetate, $CCl_3CO_2Et$ ..	2·149	8·4	459	—
Benzoic chloride, $PhCOCl$ .....	3·966	14·7	459	—
Benzylidene chloride, $PhCHCl_2$ ..	3·95	12·8	527	154·25
Bromine, $Br_2$ .....	2·393	22·3	329	—
Ethyl bromide, $EtBr$ .....	3·148	20·5	265	77·07
Propyl bromide, $Pr^aBr$ .....	3·17	16·3	293	—
Isopropyl bromide, $Pr^iBr$ .....	3·125	15·8	275	—
Allyl bromide, $C_3H_5Br$ .....	3·251	18·8	289	—
Isobutyl bromide, $C_4H_9Br$ .....	3·103	13·1	311	118·39
Isoamyl bromide, $C_5H_{11}Br$ .....	3·06	11·0	347	138·63
Bromobenzene, $C_6H_5Br$ .....	3·219	13·4	394	119·88
Bromotoluene, 1:2 $C_6H_4BrMe$ ..	3·133	11·0	425	141·95
Ethylene bromide, $C_2H_4Br_2$ .....	2·654	13·6	407	97·65
Propylene bromide, $C_3H_6Br_2$ .....	2·543	10·7	409	—
Methyl iodide, $MeI$ .....	2·532	18·5	—	—
Ethyl iodide, $EtI$ .....	2·539	14·7	316	86·12
Propyl iodide, $Pr^aI$ .....	2·574	12·0	348	—
Isopropyl iodide, $Pr^iI$ .....	2·529	11·7	331	—
Allyl iodide, $C_3H_5I$ .....	2·625	13·0	340	—
Isobutyl iodide, $C_4H_9I$ .....	2·533	9·9	366	128·28
Isoamyl iodide, $C_5H_{11}I$ .....	2·472	8·2	377	151·05
Iodobenzene, $C_6H_5I$ .....	2·674	10·2	424	130·55
Propylamine, $NH_2Pr^a$ .....	5·696	33·4	—	85·61
Allylamine, $C_3H_5NH_2$ .....	5·907	37·8	—	78·38
Isobutylamine, $C_4H_9NH_2$ .....	5·218	24·6	—	106·76
Amylamine, $C_5H_{11}NH_2$ .....	4·936	19·4	—	126·84
Diethylamine, $NHEt_2$ .....	4·986	22·9	—	109·05
Triethylamine, $NEt_3$ .....	4·205	13·7	—	153·82
Aniline, $NH_2Ph$ .....	5·405	25·5	414	106·08
Pyridine, $C_5H_5N$ .....	5·549	31·1	—	89·39
Piperidine, $C_5H_{11}N$ .....	5·303	24·4	—	108·76
Quinoline, $C_9H_7N$ .....	4·833	17·2	518	139·75
Nitromethane, $MeNO_2$ .....	5·087	42·5	361	59·5
Nitroethane, $EtNO_2$ .....	4·578	28·5	—	80·25
Nitrobenzene, $PhNO_2$ .....	5·35	17·3	419	—
Chloropicrin, $CCl_3NO_2$ .....	2·828	12·7	333	—
Ethyl nitrate, $EtONO_2$ .....	4·33	23·5	355	—
Isoamyl nitrate, $C_5H_{11}ONO_2$ .....	3·612	11·8	376	152·59
Methyl nitrite, $MeCN$ .....	6·047	52·8	—	57·23
Ethyl nitrite, $EtCN$ .....	5·452	34·8	—	78·23
Isobutyl nitrite, $C_4H_9CN$ .....	4·9	20·4	412	119·7
Amyl nitrite, $C_5H_{11}CN$ .....	4·647	16·4	448	141·1

Liquid.	$\alpha^2$ in mm.	$N = \frac{\alpha^2}{2v}$	T.	Molecular volume.
Phenyl nitrite, PhCN.....	5.0	20.6	474	—
Carbon bisulphide, CS <sub>2</sub> .....	4.747	38.2	271.5	62.05
Allyl thiocarbimide, C <sub>3</sub> H <sub>5</sub> NCS....	4.792	21.1	437	113.13
Phenyl thiocarbimide, PhNCS....	4.339	13.1	491	113.13
Methyl thiocyanate, MeSCN.....	5.132	32.5	—	408.0
Ethyl thiocyanate, EtSCN.....	4.792	24.0	—	425.0
Ethyl sulphide, Et <sub>2</sub> S.....	4.644	19.0	—	303.0
Phosphorus trichloride, PCl <sub>3</sub> .....	3.017	16.1	—	295.0
Phosphorus oxychloride, POCl <sub>3</sub> ....	2.931	14.5	—	375.0
Ethyl phosphorus dichloride, POEtCl <sub>2</sub> .....	3.17	12.4	—	350.0
Phosphorus sulphochloride, PSCl <sub>3</sub> ..	2.952	12.7	—	371.0

*Discussion of the Results.*—At the outset the values for the atomic constants of capillarity (expressed in terms of hydrogen) are compared with those calculated from the logarithmic curve, the equation for which is given above; the data in the previous memoir (cf. *supra*), C = 2H and O = 3H, are taken as the basis. A few examples illustrative of this comparison are given, thus:—

<i>Terpene from lemons</i> , C <sub>10</sub> H <sub>16</sub> . N = 10.1. Value deduced from curve.....	= 36 H
Value calculated from above data, C <sub>10</sub> H <sub>16</sub> = 10 × 2 + 6 × 1.....	= 36 H
<i>Ethyl acetoacetate</i> , C <sub>6</sub> H <sub>10</sub> O <sub>3</sub> . N = 12.8. Value deduced from curve.....	= 31 H
Value calculated from data, C <sub>6</sub> H <sub>10</sub> O <sub>3</sub> . 6 × 2 + 10 × 1 + 3 × 3.....	= 31 H

But in some cases these two values are not concordant—a result which tends to show that the atomic capillary equivalent is variable, and is dependent on the method of arrangement of the atoms within the molecule. For example:—

Acetic acid, C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> . N = 30.6. Value deduced from curve .....	= 16 H
but C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> = 2 × 2 + 4 × 1 + 2 × 3 .....	= 14 H
Difference .....	= 2 H
Dimethylresorcinol, C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> . N = 13. Value deduced from curve .....	= 30 H
but C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> = 2 × 8 + 10 × 1 + 2 × 3 .....	= 32 H
Difference .....	= 2 H

From the determinations given above, the following values are given for the atomic capillary equivalents of different elements expressed in terms of atoms of hydrogen:—

- C = 2H (in carboxylic acids C = 3H).  
 O = 3H (in substances of ethylenic oxide type O = 0H).  
 Cl = 7H (when more than one chlorine-atom is attached to the same carbon-atom or is in the side-chain of an aromatic derivative, Cl = 6H).  
 Br = 13H.  
 I = 19H.  
 N = 0H (in primary amines).  
 „ = 1H (in secondary amines).  
 „ = 2H (in tertiary amines and nitro-compounds).  
 „ = 3H (in cyanides).  
 S = 5.5H.  
 P = 5H (when trivalent).  
 P = 4H (when pentavalent).

Then on the one hand the capillary constants can be calculated from the general curve with sufficient approximation from the simple chemical formula, and on the other a study of the phenomena of capillarity is likely to be an important auxiliary for ascertaining the chemical constitution or the relative concatenation of the atoms within the molecule.

V. H. V.

**Remarks on Schiff's Article "On the Capillarity Constants of Liquids at their Boiling Points."** By P. VOLKMANN (*Annalen*, 228, 96—111).

**Determination of Chemical Affinity in Terms of Electromotive Force.** By C. R. A. WRIGHT and C. THOMPSON (*Phil. Mag.*, 19, 1—29, 102—124, 197—214).—In most cases the electromotive force of a voltaic cell differs much from that calculated from the heat due to the chemical changes, and in some instances the current flows even in the direction opposite to that deducible from the relative heats of formation of the electrolytes; hence the authors conclude that the electromotive force must in part depend on some other additional cause. The latter is an action akin to that taking place in a thermoelectric combination, and is numerically expressible by the algebraic difference between two constants ( $k_1 - k_2$ ) respectively applicable to the two halves of the combination. The actually generated electromotive force is therefore expressed by

$$E = C_1 - C_2 = E_H + k_1 - k_2.$$

where  $C_1$  and  $C_2$  are the *voltaic* constants,  $E_H$  is the electromotive force corresponding with the difference between the heats of formation, and  $k_1$ ,  $k_2$  the corresponding *thermovoltaic* constants applicable to the respective metals. The value of the *thermovoltaic* constant is, like that of the *voltaic* constant, dependent on the condition of the metallic surface, the nature and strength of the saline solution surrounding the plate, and on the temperature. The papers describe the experimental determination of the numerical values of the *voltaic* and *thermovoltaic* constants for various kinds of two-fluid cells, in which each metallic plate was surrounded by a solution of its own sulphate,

nitrate, acetate, chloride, iodide or bromide, the acid of the salt being the same in the two halves of each combination. R. R.

**Gravitation and Atomic Weight.** By L. DULK (*Ber.*, 18, 432—438).

**Possibility of Several Structural Formulæ for the same Chemical Compound.** By C. LAAR (*Ber.*, 18, 648—657).

**New Apparatus for the Constant Production of Gas.** By G. TISSANDIER (*Bull. Soc. Chim.*, 43, 233—236).

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## Inorganic Chemistry.

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**Time of Existence of Thiosulphuric Acid in Aqueous Solution.** By A. WINKELMANN (*Ber.*, 18, 406—410).—A reply to Landolt (*Abstr.*, 1884, 554).

**Preparation of Ammonia Gas.** By ISAMBERT (*Compt. rend.*, 100, 857—859).—The decomposition of ammonium chloride by calcium oxide is an endothermic reaction, and the same is true of the reaction between lead monoxide and ammonium chloride. The action of barium oxide on ammonium chloride, on the other hand, is exothermic, but no sensible decomposition takes place at the ordinary temperature. If the mixture is heated, ammonia gas is rapidly given off at 180—200°.

Ammonia can be readily prepared from the dihydrosulphide, or the anhydrous carbonate, which possess a considerable tension of dissociation even at the ordinary temperature, by bringing them in contact with some substance which will combine with the acid. It seems probable, therefore, that ammonium chloride behaves in a similar manner, and undergoes dissociation, the base which is present combining with the liberated acid, whilst the ammonia remains in the free state. This is supported by the fact that zinc chloride, which can absorb ammonia gas at a high temperature, rapidly decomposes ammonium chloride at this temperature with liberation of hydrogen chloride, a reaction strictly analogous to that between ammonium dihydrosulphide and water. It follows that in considering the action of anhydrous bases on ammonium chloride, the heat developed by the union of ammonia with hydrochloric acid need not be taken into account.

C. H. B.

**Formation of Hydroxylamine by the Action of Potassium Nitrite on Hyposulphurous Acid.** By A. LIDOFF (*Jour. Russ. Chem. Soc.*, 1884, 751—754).—On pouring potassium nitrite into the

solution of hyposulphite obtained by the action of sulphurous acid on zinc, a considerable amount of gas is evolved on shaking the liquid, but no brown vapours of oxides of nitrogen are formed. The liquid thus obtained gives an abundant precipitate of cuprous oxide with Lossen's reagent (cupric oxide and caustic potash), and as neither sulphites nor nitrites give this reaction there can be no doubt that a hydroxylamine salt is present. Its formation may be explained by the oxidation of the hyposulphurous acid to sulphuric acid, whilst the nitrous acid is itself converted into the base. Hydroxylamine sulphate was separated from the mixture of sulphates and sulphites of zinc, potassium, ammonium, and hydroxylamine, by first oxidising the sulphites to sulphates by means of a current of air, then precipitating the zinc salt with excess of potassium carbonate, neutralising the liquid with sulphuric acid, and repeatedly evaporating and crystallising the potassium and ammonium sulphates; finally, on evaporating to dryness hydroxylamine sulphate was obtained, contaminated of course with ammonium sulphate and thiosulphate, the latter being formed by decomposition of hyposulphurous acid. The reaction may be represented as follows:  $2\text{H}_2\text{SO}_3 + 2\text{KNO}_2 + 2\text{H}_2\text{O} = (\text{NH}_3\text{O})_2\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4$ . The evolution of gas in the beginning is probably due to the decomposition of hydroxylamine by nitrous acid into water and nitrogen monoxide. A. T.

**Compounds of Arsenious Anhydride with Potassium Bromide and Iodide.** By H. SCHIFF and R. SESTINI (*Annalen*, 228, 72—91).—After referring to the compounds of arsenious oxide with potassium iodide, discovered by J. P. Emmet (*Silliman's Journal*, 18, 58) and E. Harms (*Ann.*, 91, 171), the authors describe the formation of analogous compounds by the action of potassium iodide on potassium arsenite or arsenious oxide, and by the action of iodine on potassium arsenite. The product dissolves in 40 parts by weight of cold and 20 of hot water, and consists in all probability of a mixture of two salts,  $4\text{As}_2\text{O}_3, 2\text{KI}$  and  $4\text{As}_2\text{O}_3, 2\text{KI} + \text{H}_2\text{O}$ . W. C. W.

**Presence of Chlorine in Potassium Bromide.** By T. WEIGLE (*Chem. Centr.*, 1885, 145).—Certain samples of potassium bromide which had been heated to redness to expel moisture, were found to precipitate more silver solution than portions of the same samples only heated to  $100^\circ$ . Investigation showed the presence of potassium chlorate in the original samples. J. K. C.

**Preparation of Sodium Hyposulphite.** By G. S. MANZONI (*Gazzetta*, 14, 361—362).—It is here suggested that the copper-zinc couple may conveniently replace zinc in Schützenberger's process for the preparation of sodium hyposulphite. V. H. V.

**Combination of Ammonia with Ammonium Salts.** By G. PELLIZZARI (*Gazzetta*, 14, 362—368).—In the course of investigations on the benzylic ether of the dihydroxybenzenes, it was observed that benzyldinitroquinol formed two compounds with ammonia, the one stable, containing 1 mol.  $\text{NH}_3$ , the other unstable, containing 2 mols.

$\text{NH}_3$ , and existing only in an atmosphere of that gas (Abstr., 1884; 438). This result taken in connection with Divers' observation that ammonium nitrate absorbs ammonia with formation of a liquid compound, led the author to determine the proportion of ammonia absorbed by various carbon compounds. As a general result, it may be stated that monhydroxyphenols and carboxylic acids containing a nitro-group, or several chlorine-atoms, and in the case of the latter, an hydroxyl-group, tend to absorb a quantity of ammonia which corresponds with the combination of 2 mols. of the gas with 1 mol. of the substance in question. Of such examples may be cited trinitro- and trichloro-phenols, the meta- and para-hydroxybenzoic acids, and nitro-salicylic acid. Blondeau's experiments on the absorption of ammonia by pyroxylin were repeated; these tended to show that a triamido-trinitro-cellulose was formed, but, although the formation of unstable ammonia derivatives similar to those described above, was confirmed, yet it was not found possible to determine the composition of the products, inasmuch as the phenomenon was complicated by the formation of ammonium nitrate, and the consequent absorption of ammonia by this substance.

V. H. V.

**New Crystallised Magnesium Phosphate, and the corresponding Arsenate.** By A. DE SCHULTEN (*Compt. rend.*, 100, 877—879).—When a solution of magnesium carbonate in an excess of phosphoric acid is heated in sealed tubes at  $225^\circ$  for some hours, the phosphate,  $\text{HMgPO}_4 + \text{H}_2\text{O}$ , is obtained in microscopic crystals easily soluble in warm dilute acids; sp. gr. = 2.326 at  $15^\circ$ ; this compound has the same percentage composition as the pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7 + 3\text{H}_2\text{O}$ , obtained by Schwarzenberger, but the latter loses all its water at  $100^\circ$ , whilst the orthophosphate obtained by the author undergoes no change at this temperature. The phosphate forms thin, somewhat elongated hexagonal lamellæ, which agree in some of their properties with orthorhombic crystals, but probably consist of four monoclinic crystals maced along  $g'$ , with the plane of their optical axes perpendicular to the plane of symmetry.

If arsenic acid is employed in place of phosphoric acid, the arsenate,  $2\text{HMgAsO}_4 + \text{H}_2\text{O}$ , is obtained in small prismatic crystals, very probably monoclinic. This arsenate resembles many other arsenates in containing 2 mols. of the salt combined with 1 mol.  $\text{H}_2\text{O}$ .

C. H. B.

**Magnesium Hydrocarbonate.** By R. ENGEL (*Compt. rend.*, 100, 911—913).—The amorphous precipitate formed when an alkaline carbonate is added to a solution of a magnesium salt has the composition  $\text{MgCO}_3 + 2\text{H}_2\text{O}$ , but after one or two hours, below  $16^\circ$ , it becomes converted into tabular crystals of the composition  $\text{MgCO}_3 + 5\text{H}_2\text{O}$ . If the temperature is above  $22^\circ$ , it is converted into prismatic crystals of the composition  $\text{MgCO}_3 + 3\text{H}_2\text{O}$ , and between  $16^\circ$  and  $22^\circ$  into a mixture of both compounds.

The amorphous precipitate is decomposed by water, and converted into  $5\text{MgO}, 4\text{CO}_2 + 11\text{H}_2\text{O}$ , or  $5(\text{MgCO}_3 + 2\text{H}_2\text{O})$  in which 1 mol.  $\text{MgCO}_3$  has been converted into  $\text{MgH}_2\text{O}_2$ . This product differs from the



hydrocarbonate obtained in hot solutions, both in composition and in properties. It dissolves to an appreciable extent in a solution of magnesium hydrogen carbonate, and, if the latter is in excess, is rapidly and completely converted into the normal carbonate; it also absorbs carbonic anhydride from the atmosphere with the same result.

Normal magnesium carbonate is not converted into the hydrocarbonate in presence of alkaline carbonates at the ordinary temperature, and on the other hand the hydrocarbonate of pharmacy precipitated from hot solutions is not converted into the normal carbonate in presence of alkaline hydrogen carbonates, or magnesium hydrogen carbonate.

C. H. B.

**Basic Lead Nitrates.** By A. SMOLKA (*Monatsh. Chem.*, **6**, 195—197).—The author proves by analysis that the basic lead nitrate,  $\text{Pb}_5\text{H}_5\text{N}_5\text{O}_{15}$ , which Morawski (Abstr., 1881, 145) obtained from plumbonitroglyceride is not identical with the salt described by Loewe (*J. pr. Chem.*, **98**, 388), which has the composition  $6\text{PbO}, 2\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ .

W. C. W.

**Preparation of Chromium and Aluminium Sulphites.** By G. S. MANZONI (*Gazzetta*, **14**, 360—361).—Aluminium and chromium sulphites are conveniently prepared by heating together concentrated solutions of aluminium sulphate or chromium potassium sulphate with sodium sulphite. The soluble sulphites are separated from the less soluble sulphates by fractional crystallisation.

V. H. V.

**Behaviour of the Different Modifications of Carbon towards Iron at an Elevated Temperature.** By W. HEMPEL (*Ber.*, **18**, 998—1001).—In these experiments, the author employed commercial malleable iron-foil containing 0.021 per cent. carbon, 0.04 per cent. silicon, and 0.336 per cent. manganese; the diamonds were perfectly colourless, and were previously heated to redness in an atmosphere of nitrogen; the amorphous carbon was obtained by gradually heating chemically pure sugar to a white heat. A comparative experiment is described, in which a piece of foil was covered at one end with amorphous carbon, in the middle with diamond-dust, and at the other end with graphite (crystallised from cast iron); the whole was heated for about two hours in a current of nitrogen to the highest temperature of a combustion furnace, after which treatment the iron was found to be unaltered. At the somewhat higher temperature of a blowpipe, the iron was converted into white iron where it was in contact with the diamond, whilst those portions covered with amorphous carbon and graphite appeared to be unaltered. The lowest temperature at which carburisation takes place with the diamond is estimated (by Prinsep's method) at  $1160^\circ$ . The carburisation by means of amorphous carbon was effected in a Schlösing's furnace, and the lowest temperature at which grey iron is formed estimated at  $1385^\circ$  to  $1420^\circ$ . On exposing iron placed between carbon poles (in an atmosphere of nitrogen) to the temperature of the electric arc, white iron is produced.

The different behaviour of the diamond and of amorphous carbon

towards iron is compared to that of white and amorphous phosphorus to solvents.

A. K. M.

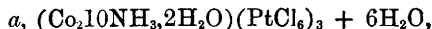
**Roseocobalt Salts.** By S. M. JÖRGENSEN (*J. pr. Chem.* [2], 31, 49—93).—In continuation of the author's work on these salts (this vol., p. 23) roseocobalt nitrate,  $(\text{Co}_2\text{10NH}_3\cdot 2\text{H}_2\text{O})(\text{NO}_3)_6$ , is converted into nitrato-purpureo nitrate by drying at  $100^\circ$  for an hour; dilute nitric acid precipitates this compound from its moderately concentrated solutions.

*Roseocobalt nitrate sulphate*,  $(\text{Co}_2\text{10NH}_3\cdot 2\text{H}_2\text{O})(\text{SO}_4)_2(\text{NO}_3)_2$ , is obtained either by dissolving roseocobalt sulphate in warm nitric acid, when it separates out on cooling, or by adding dilute sulphuric acid to a solution of roseocobalt nitrate, when it forms a red precipitate consisting of microscopic octohedrons much resembling the roseo-sulphate.

*Roseocobalt platinochloride nitrate*,  $(\text{Co}_2\text{10NH}_3\cdot 2\text{H}_2\text{O})(\text{NO}_3)_2(\text{PtCl}_6)_2 + 2\text{H}_2\text{O}$ , is obtained as a brownish-red crystalline precipitate on adding hydrogen platinochloride in theoretical amount to a dilute solution of roseocobalt nitrate. When dried for 48 hours at  $100^\circ$ , this salt is converted into the nitrato-purpureo chloride.

*Roseocobalt chloride*,  $(\text{Co}_2\text{10NH}_3\cdot 2\text{H}_2\text{O})\text{Cl}_6$ , is converted into the chloropurpureo chloride on drying.

There are three different roseocobalt platinochlorides,



prepared by precipitating a solution of roseocobalt chloride with a neutral solution of sodium platinochloride, when it forms a lustrous crystalline precipitate of thin four- or eight-sided tablets; *b*,  $(\text{Co}_2\text{10NH}_3\cdot 2\text{H}_2\text{O})\text{Cl}_2(\text{PtCl}_6)_2 + \text{H}_2\text{O}$ , is prepared by treating an aqueous solution of roseocobalt chloride with the theoretical quantity of hydrogen platinochloride, when it is obtained as a reddish-brown crystalline precipitate; *c*,  $(\text{Co}_2\text{10NH}_3\cdot 2\text{H}_2\text{O})\text{Cl}_4\text{PtCl}_6 + 2\text{H}_2\text{O}$ , is prepared by mixing a solution of hydrogen platinochloride, with a solution of roseocobalt chloride acidulated with hydrochloric acid, and then shaking the mixture with half its volume of absolute alcohol; it then forms a brick-red crystalline precipitate consisting of microscopic rhombic tablets.

*Roseocobalt mercuriochlorides*: *a*,  $(\text{Co}_2\text{10NH}_3\cdot 2\text{H}_2\text{O})\text{Cl}_4(\text{HgCl}_3)_2$ , is obtained in the same manner as the corresponding luteo-salt, as a bright red crystalline precipitate; by dissolving this salt in warm sulphuric acid and afterwards cooling, the second mercuriochloride, *b*,  $(\text{Co}_2\text{10NH}_3\cdot 2\text{H}_2\text{O})(\text{HgCl}_3)_6 + 2\text{H}_2\text{O}$ , is obtained.

*Roseocobalt bromide*,  $(\text{Co}_2\text{10NH}_3\cdot 2\text{H}_2\text{O})\text{Br}_6$ , gives reactions similar to those of the nitrate and chloride; it is obtained by precipitating roseocobalt nitrate with hydrobromic acid, as a red crystalline precipitate of rhombic tablets; when heated at  $100^\circ$ , it loses water and is converted into bromopurpureo bromide.

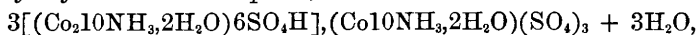
*Roseocobalt bromide disulphate*,  $(\text{Co}_2\text{10NH}_3\cdot 2\text{H}_2\text{O})\text{Br}_2(\text{SO}_4)_2$ , is obtained by dissolving roseocobalt bromide in sulphuric acid, when a granular crystalline precipitate separates after a time.

*Roseocobalt platinobromides*: *a*,  $(\text{Co}_2\text{10NH}_3\cdot 2\text{H}_2\text{O})\text{Br}_2(\text{PtBr}_6)_2 +$

$2\text{H}_2\text{O}$ , is prepared by adding a solution of sodium platinobromide to a solution of roseocobalt bromide, and is obtained as a precipitate of dark red prisms having much the appearance of crystals of chromic acid; it is not decomposed on solution in water, like the corresponding platinochloride. When dried at  $100^\circ$ , it is converted into bromopurpureocobalt platinobromide. *b*,  $(\text{Co}_2\cdot 10\text{NH}_3\cdot 2\text{H}_2\text{O})(\text{PtBr}_6)_3 + 4\text{H}_2\text{O}$ , is obtained as a scarlet crystalline precipitate on decomposing the chloride with sodium platinobromide.

*Roseocobalt iodide*,  $(\text{Co}_2\cdot 10\text{NH}_3\cdot 2\text{H}_2\text{O})\text{I}_6$ , obtained by the action of hydriodic acid on the hydroxide or carbonate, forms a dark red precipitate, consisting of minute octohedrons and six-sided tables.

*Hydrogen roseocobalt sulphate*,



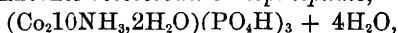
is prepared by dissolving cobalt carbonate in dilute sulphuric acid, adding to this solution an excess of ammonium hydroxide, and after 48 hours passing a rapid stream of air through the liquid. Sulphuric acid is then added, when this salt is obtained in octohedral crystals; it is rapidly decomposed by water into the normal sulphate and free sulphuric acid.

*Normal roseocobalt sulphate*,  $(\text{Co}_2\cdot 10\text{NH}_3\cdot 2\text{H}_2\text{O})(\text{SO}_4)_3 + 3\text{H}_2\text{O}$ , is obtained from the acid salt by crystallisation from an aqueous solution, or by treating a solution of roseocobalt carbonate with an excess of sulphuric acid; it is sparingly soluble in water. This salt is easily broken up into the tetramine and luteo-salts, and on this account the author considers that the formula should be twice that above given.

*Roseocobalt platinochloride sulphate*,  $(\text{Co}_2\cdot 10\text{NH}_3\cdot 2\text{H}_2\text{O})(\text{PtCl}_6)(\text{SO}_4)_2$ , is prepared by adding hydrogen platinochloride to an aqueous solution of roseocobalt sulphate acidulated with sulphuric acid, when it separates in brilliant reddish-yellow six-sided tablets; it is but little soluble in water.

*Roseocobalt aurochloride sulphate*,  $(\text{Co}_2\cdot 10\text{NH}_3\cdot 2\text{H}_2\text{O})(\text{AuCl}_4)(\text{SO}_4)_2$ , is obtained by treating the aqueous solution of roseocobalt chloride with a solution of hydrogen aurochloride and sulphuric acid, when an abundant orange-red precipitate is obtained consisting of rectangular prisms, which under the microscope appear slightly dichroic.

*A basic roseocobalt orthophosphate*,  $(\text{Co}_2\cdot 10\text{NH}_3\cdot 2\text{H}_2\text{O})(\text{OH})_2(\text{PO}_4\text{H})_2 + 2\text{H}_2\text{O}$ , is obtained on treating the basic roseo nitrate with normal sodium phosphate; it separates in dark red prisms almost insoluble in cold water. Another *roseocobalt orthophosphate*,



is obtained by treating a solution of roseocobalt carbonate with a 10 per cent. solution of phosphoric acid; it forms a crystalline precipitate much resembling in appearance the corresponding luteo-compound; it is very slightly soluble in cold water, but more so in hot; on heating gently, it melts below  $100^\circ$ , and forms a sticky reddish-brown mass which on cooling becomes brittle, and of a clear red colour; it is easily soluble in hydrochloric acid.

*Sodium roseocobalt pyrophosphate*,  $(\text{Co}_2\cdot 10\text{NH}_3\cdot 2\text{H}_2\text{O})(\text{P}_2\text{O}_7\text{Na})_2 + 23\text{H}_2\text{O}$ , is obtained by acting on a solution of roseocobalt sulphate with

sodium pyrophosphate, as an amorphous precipitate; this is soluble in excess of the sodium pyrophosphate, and is reprecipitated in the crystalline form on shaking.

*Normal roseocobalt pyrophosphate*,  $(\text{Co}_210\text{NH}_3, 2\text{H}_2\text{O})_2(\text{P}_2\text{O}_7)_3 + 12\text{H}_2\text{O}$ , is obtained by the precipitation of roseocobalt sulphate with the theoretical quantity of sodium pyrophosphate; it is crystalline and is not altered on drying or exposure to the air.

*Roseocobalt cobalticyanide*,  $(\text{Co}_210\text{NH}_3, 2\text{H}_2\text{O})\text{Co}_2\text{Cy}_{12}$ , is prepared by acting on an acid solution of chloropurpureocobalt chloride, with a slight excess of potassium cobalticyanide, and is obtained as a crystalline precipitate in almost theoretical quantity; it is almost insoluble in cold water. A. P.

**New Tin Salts.** By T. BENAS (*Chem. Centr.*, 1884, 957—958).—The author describes the salts,  $\text{SnCl}_2, \text{KCl} + \text{H}_2\text{O}$ , and  $\text{SnCl}_2, 2\text{KCl} + \text{H}_2\text{O}$ , which are prepared by the reaction of a strong solution of stannous chloride with a saturated solution of potassium chloride. The second salt is only formed in presence of strong hydrochloric acid, and is transformed into the first salt by treatment with water.

*Stannous bromide*.—Stannous bromide was prepared by dissolving tin in boiling concentrated hydrobromic acid (sp. gr. 1.48). The greenish-yellow solution on cooling deposits colourless doubly refractive needles of  $\text{SnBr}_2 + \text{H}_2\text{O}$ ; it oxidises in moist air, and loses its water of crystallisation when exposed to dry air, or by prolonged heating at  $70-80^\circ$ . The salt dissolves in a small quantity of water to a clear solution, but is decomposed by excess, forming a gelatinous white precipitate. Crystals of  $\text{SnBr}_2 + 2\text{H}_2\text{O}$  were also deposited from the original solution in large monoclinic tables, which easily change into the monohydrate. Stannous bromide combines with the bromides of the alkali metals to form double salts. Of these,  $\text{SnBr}_2, \text{KBr} + \text{H}_2\text{O}$ ;  $\text{SnBr}_2, 2\text{NH}_4\text{Br} + \text{H}_2\text{O}$ , and  $\text{SnBr}_2, \text{NH}_4\text{Br} + \text{H}_2\text{O}$ , were prepared. W. R. D.

**Compounds of Platinum and Arsenic.** By D. TIVOLI (*Gazzetta*, 14, 487—491).—By passing a rapid current of arsenic hydride into a solution of platinum chloride, there are formed minute black crystalline scales of a *hydroxyarsenide of platinum* in accordance with the equation  $\text{PtCl}_4 + \text{AsH}_3 + \text{H}_2\text{O} = \text{PtAs}\cdot\text{OH} + 4\text{HCl}$ . This substance is insoluble in water, and only altered to a slight extent by hydrochloric and nitric acids and potash; it is readily soluble in aqua regia. Concentrated sulphuric acid decomposes it in accordance with the equation  $2\text{PtAs}\cdot\text{OH} + 2\text{H}_2\text{SO}_4 = \text{Pt} + \text{As}_2\text{O}_3 + 3\text{H}_2\text{O} + 2\text{SO}_2$ . It may be dried at  $130^\circ$  without decomposition, but above that temperature is transformed into a platinum arsenide thus:  $6\text{PtAs}\cdot\text{OH} = \text{As}_2\text{O}_3 + 2\text{Pt}_3\text{As}_2 + 3\text{H}_2\text{O}$ . These two decompositions served as a basis for the analysis of platinum hydroxyarsenide. V. H. V.

## Mineralogical Chemistry.

**The Coefficients of Elasticity of Crystals.** By J. BECKENKAMP (*Zeit. Kryst. Min.*, 10, 41—57).—Koch has determined the coefficients of elasticity for rods of rock salt, sylvine, and sodium chlorate, cut perpendicularly to the faces of the dodecahedron, and perpendicularly to the faces of the cube (Abstr., 1884, 1096). His final results were as follows:—

	$E_1$ .	$E_3$ .	$\frac{E_1}{E_3}$ .
Sylvine.....	4010	2088	1.92
Rock salt.....	4030	3395	1.19
Sodium chlorate....	4047	3190	1.27

The author's experiments give the corresponding values for—

Alum .....	1793	1998	0.90
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From his investigations he draws the following conclusions:—In all directions which are crystallographically identical, the elasticity is the same. The elasticity of alum is less than that of all other known crystals. This fact explains the anomalous double refraction of alum, as even small mechanical forces, during the crystallisation, give rise to great molecular displacements. The ratio  $\frac{E_1}{E_3}$  of the refractive indices is nearer unity in the case of alum than in other crystals. In the latter case,  $E_3$  is less than  $E_1$ , whilst with alum  $E_3$  is greater than  $E_1$ . The constant decrease of the coefficient of elasticity with repeated load is remarkable. Perhaps this bears some relation to the observation made by Wiedemann, that even at 50° alum is subject to a molecular change. The hemihedral symmetry of the elasticity could not be observed in alum. Assuming that Neumann's formula holds good for alum, the following results are obtained:—

	$E_1$ , perpendi- cular to $\infty 0 \infty$ .	$E_2$ , perpendi- cular to $\infty 0 2$ .	$E_3$ , perpendi- cular to $\infty 0$ .	$E_4$ , perpendi- cular to 0.
Calculated..	1806	1892	1987	2057
Observed ..	1793	1894	1998	2035

B. H. B.

**Conditions for the Formation of Native Sulphur.** By L. ILOSVAY (*Zeit. Kryst. Min.*, 10, 91—93).—In the gases of active volcanos,  $H_2S$  and  $SO_2$  occur. The author has endeavoured to determine to what chemical changes these products are submitted when they arrive at the surface of the earth at the same time. The answer is, that the hydrogen of the  $H_2S$  very easily forms water by combining with the oxygen of various oxygen compounds. For this reason sulphurous anhydride gives up its oxygen, and consequently sulphur

is liberated from both compounds. This change is easily effected at a high temperature, in the presence of aqueous vapour. If, however, but one of these conditions is fulfilled, and only aqueous vapour is present, this would be sufficient for the sulphur to be liberated. And as sulphur is never met with at a great depth, the author is of opinion that sulphur is formed at the ordinary temperature, or at a temperature not much higher.

B. H. B.

### Native Mercury, Cinnabar, and Chromium Ores from Servia.

By F. SCHAFARZIK (*Zeit. Kryst. Min.*, 10, 93).—These minerals were found at Suplja Sztena, in the Avala Mountains, near Belgrade, in a quartzite vein at the contact of serpentine and marl. The vein was filled with chrome-iron ore and iron pyrites, together with chrome ochre and iron ochre formed by their oxidation. In several fissures in the vein, barytes crystals occur, covered by a subsequent deposit of quartz. In cavities in the quartz, cinnabar occurs; it also appears to be disseminated through the rock itself. Between the cinnabar crystals, drops of native mercury are met with. The cinnabar crystals were transparent, and of a cochineal-red colour. The author observed the following forms:— $0R$ ,  $R$ ,  $\infty R$ ,  $\frac{2}{3}R$ , and two negative rhombohedra.

B. H. B.

### Orpiment and Realgar from Bosnia.

By J. A. KRENNER (*Zeit. Kryst. Min.*, 10, 90—91).—Orpiment and realgar occur at Kreševo (Bosnia), implanted on quartz crystals in a greyish micaceous phyllite. The realgar is of later formation, and is often implanted on the orpiment. The orpiment crystals are either separate or united, forming druses. They have a wax-yellow colour on the surface, whilst the pure citron-yellow appears on the fresh cleavage planes. The following planes were determined:— $\infty P\infty$ ,  $\infty \bar{P}\infty$ ,  $\infty P$ ,  $\infty \bar{P}7$ ,  $\infty P\frac{1}{2}$ ,  $\infty \bar{P}2$ ,  $\bar{P}\infty$ .

The crystals of realgar usually occur as thick tabular forms, 4 mm. long, and are either transparent and red, or brownish-black and opaque. The author determined 20 planes, of which the three following are new:— $\infty P\frac{2}{3}$ ,  $P\frac{4}{3}$ ,  $2P2$ .

B. H. B.

### Smithsonite from Pelsöcz Ardó.

By J. LOCZKA (*Zeit. Kryst. Min.*, 10, 89).—The analysis gave the following results:—

ZnO.	CaO.	PbO.	CdO.	MgO.	CO <sub>2</sub> .	Total.	Density.
63.23	1.01	0.75	0.02	trace	34.69	99.70	4.43

B. H. B.

### Colemanite.

By T. HIORTDAHL (*Zeit. Kryst. Min.*, 10, 25—31).—The author's analysis of colemanite from California (I) agrees very well with the results obtained by Price (II).

	B <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> .	MgO.	Total.
I.	47.64	27.97	22.79	1.28	0.19	0.13	100.00
II.	48.12	28.43	22.20	0.65	0.60	—	100.00

These figures correspond with the formula  $Ca_3B_5O_{15} + 7H_2O$ . The mineral is monoclinic. The following forms were determined:—

$\infty P\infty$ ,  $\infty P\infty$ ,  $0P$ ,  $\infty P$ ,  $\infty P2$ ,  $\infty P2$ ,  $P\infty$ ,  $2P\infty$ ,  $-2P\infty$ ,  $+P\infty$ ,  $+2P\infty$ ,  $-P$ ,  $-3P$ ,  $-3P3$ ,  $-3P3$ ,  $+P$ ,  $+2P$ ,  $+2P2$ ,  $+3P\frac{3}{2}$ ,  $+2P2$ . The axial ratio was calculated to be  $a : b : c = 0.7747 : 1 : 0.5418$ .  $\beta = 69^\circ 47'$ . (Comp. this volume, pages 224 and 358.) B. H. B.

**New Locality for Vivianite Crystals.** By A. KOCH (*Zeit. Kryst. Min.*, 10, 94—95).—Two years ago the author obtained two remarkably fine crystals of vivianite from one of the Vöröspatak mines. The forms observed were:— $P$ ,  $P\infty$ ,  $\infty P$ ,  $\infty P\infty$ ,  $\infty R\infty$ . B. H. B.

**Optical Properties of Allactite.** By J. KRENNER (*Zeit. Kryst. Min.*, 10, 83—85).—Sjögren has recently described, under the name of allactite, a new mineral from Nordmarken. The crystals belong to the monoclinic system, the axial ratio being

$$a : b : c = 0.6115 : 1 : 0.3315. \quad \beta = 84^\circ 16' 5'.$$

With regard to its optical properties, Sjögren determined the indices of refraction for red, yellow, and violet. The plane of the optic axes is parallel to the plane of symmetry for red and yellow. The author now shows that in blue light, however, the plane of the optic axes is perpendicular to the plane of symmetry, or parallel to the ortho-axis. The apparent optic axial angle measured at  $19.4^\circ \text{C}$ . in oil is as follows:—

$$\begin{aligned} 2H_a &= 12^\circ 22' \text{ red (red glass),} \\ &= 9 \quad 12 \text{ yellow (sodium flame),} \\ &= 0 \quad 0 \text{ green (thallium flame),} \\ &= 11 \quad 36 \text{ blue (cuprammonium oxide).} \end{aligned}$$

The apparent dispersion of the axes is consequently  $23^\circ 58'$ . Adopting the mean indices of refraction given by Sjögren—

$$\begin{aligned} \beta &= 1.778 \text{ red,} \\ &= 1.786 \text{ yellow,} \end{aligned}$$

the actual axial angle is—

$$\begin{aligned} 2V_a &= 10^\circ 12' \text{ red,} \\ &= 7 \quad 34 \text{ yellow.} \end{aligned}$$

By the discovery of allactite, an addition is made to the small number of minerals that change the position of the optic axial plane for the opposite ends of the spectrum.

In conclusion, the author objects to the classification of this mineral with the vivianite group. The cleavage of allactite is quite different from that of the members of that small but sharply defined mineral group. Rammelsberg (*Abstr.*, 1884, 1097) has also raised objections from a chemical point of view. B. H. B.

**Cuprodescloizite.** By C. RAMMELSBURG (*Chem. Centr.*, 1884, 146).—In a previous paper (*Abstr.*, 1881, 1000), the author described the properties of descloizite, a vanadate of the formula  $(\text{PbZn})_4\text{V}_2\text{O}_9 + \text{Aq}$ . In the present paper a new vanadate found, accompany-

ing calcespar, at St. Louis Potosi, Mexico, is described. It forms blackish, indistinctly crystalline kidney-shaped masses, which yield a brown powder. Density 5.856. The new mineral melts easily, and dissolves in nitric acid, forming a green solution. It is a hydrous vanadate of lead, zinc, and copper containing small quantities of phosphoric and arsenic acids.

$P_2O_5$ .	$As_2O_5$ .	$V_2O_5$ .	$PbO$ .	$ZnO$ .	$CaO$ .	$H_2O$ .
0.17	0.28	22.47	54.57	12.75	8.26	2.52

Hence the new mineral is quite analogous to descloizite. It is a vanadate of the general formula  $R_4U_2O_9 + Aq$ , and may be represented as descloizite in which three-eighths of the zinc is replaced by copper ( $PbZnCu_3V_2O_9$ ), whence the name *cuprodescloizite*.

The same elements are present in the tritochlorite of Frenzel ( $R_3V_2O_9$ ). Mottramite, psittacinite, and a mineral from Laurium are lead and copper vanadates. The constitution of the first of these is uncertain; the two latter appear to belong to the same group of vanadates as tritochlorite.

W. R. D.

**Columbite from Craveggia, in Piedmont.** By J. STRÜVER (*Zeit. Kryst. Min.*, 10, 85—86).—Spezia described (Abstr., 1883, 958) a new occurrence of beryl at Craveggia. Associated with the beryl, the author has discovered minute black crystals. One of these crystals exhibited the following combination:  $\infty P\infty$ ,  $\infty \bar{P}\infty$ ,  $0P$ ,  $\infty P$ ,  $\infty \bar{P}3$ ,  $\infty P5$ ,  $\bar{P}\infty$ ,  $P$ ,  $2\bar{P}2$ .

The author concludes that the mineral is columbite, a mineral hitherto never met with in Italy or the Alps.

B. H. B.

**Microlite.** By C. HINTZE (*Zeit. Kryst. Min.*, 10, 86).—Microlite from various localities is always stated to belong to the regular system, but no precise optical examination has, up to the present time, been made. For the purpose of this examination, the author employed three sections, parallel to the three planes of the cube, from an unweathered specimen of the microlite crystals from Amelia Co., Virginia, described by Dunnington (Abstr., 1881, 1002). From the behaviour of the three crystal plates, the author concludes that microlite must be regarded as an undoubtedly regular mineral.

B. H. B.

**Astracanite.** By V. MARKOWNIKOFF (*J. Russ. Chem. Soc.*, 1884 [1], 690—694).—The first analysis of salt deposited in one of the bitter lakes of the Government of Astrakhan was made by Höbel, who found it to contain about 41 per cent. of sodium sulphate: hence G. Rose deduced the formula  $Na_2SO_4MgSO_4 + 4H_2O$  for the mineral, and gave it the name astracanite. This was contradicted by Fedchenko in 1870, who analysed the salt of some of these lakes and found its composition to vary, and never to contain so large an amount of sodium sulphate.

The author having visited the bitter lakes on the northern shore of the Caspian, found, on analysing samples of their salt, that neither the former nor the latter of these opinions is quite correct. He



states that the Little Kordouan lake, specially investigated by Fedchenko, can in nowise be considered a typical bitter lake, such lakes being situated for the most part in the south of the Kalmuck Steppe, and to the east of the Kardouan lakes, as far as the mouth of the Oural river, samples of thénardite (pure sodium sulphate) being even found in these lakes. Analysis of a sample of salt from the Great Bassine lake proved it to be pure astracanite. The colour of this mineral is generally black, from the mud enclosed in the crystals, although sometimes grey or even entirely translucent crystals, and whole layers of the mineral are met with. The purer the crystals of astracanite, the less are they subject to efflorescence. A. T.

**Barytes from Mittelagger.** By C. BUSZ (*Zeit. Kryst. Min.*, 10, 32—40).—In the Mineralogical Museum of the University of Bonn, there is a series of specimens of barytes of which no account has yet been published. The crystals come from the Alter Bleiberg Mine, near Mittelagger, in the Runderoth mining district. On the crystals, the following 13 planes were observed:— $0P$ ,  $\bar{P}\infty$ ,  $\bar{P}\infty$ ,  $\infty\bar{P}\infty$ ,  $\infty\bar{P}\infty$ ,  $\infty P$ ,  $\infty P2$ ,  $\infty P4$ ,  $P$ ,  $\frac{3}{2}P2$ ,  $5P\frac{1}{6}$ ,  $7P\frac{2}{3}$ ,  $10P\frac{1}{9}$ . The author divides the crystals into five types, which he describes and illustrates. From the angles measured on all the crystals, the axial ratio is calculated to be  $0.619278 : 1 : 0.760934$  when the longest axis is taken as unity, or  $1.61481 : 1 : 1.22876$  when the shortest axis = 1. B. H. B.

**Barytes from Pésey.** By D. FÉNYES (*Zeit. Kryst. Min.*, 10, 89—90).—An account of the crystallographic examination of barytes crystals from Pésey, Dep. Savoie, France, in the collection of the Hungarian National Museum. B. H. B.

**Anglesite from Felső-Vissó.** By A. FRANZENAU (*Zeit. Kryst. Min.*, 10, 88).—On a highly weathered mica schist from Felső-Vissó, Hungary, the author found white crystals of anglesite, on which he observed the following planes:— $0P$ ,  $\infty\bar{P}\infty$ ,  $\infty P$ ,  $\frac{1}{2}\bar{P}\infty$ ,  $\bar{P}\infty$ ,  $2\bar{P}\infty$ ,  $P$ ,  $\bar{P}5$ ,  $\bar{P}6$ ,  $\bar{P}12$ . Of these,  $\bar{P}5$  and  $\bar{P}6$  have, up to the present time, been observed only on Hungarian anglesites.  $\bar{P}12$  is a new form. B. H. B.

**Mineralogical Notes from Transylvania.** By G. PRIMICS (*Zeit. Kryst. Min.*, 10, 93—94).—The author describes the crystallographical examination of the following minerals:—1. Loose orthoclase crystals from the granite of Kis-Szamos; 2. Staurolite from the neighbourhood of Sebes, in the Fogaraser Mountains; 3. Cyanite from the same locality; 4. Tremolite from the Sebes Valley and from Boia Mica in Roumania. B. H. B.

**Nephrite from Tasmania.** By C. BODEWIG (*Zeit. Kryst. Min.*, 10, 86—87).—This mineral, which is very similar to saccharite, occurs in large quantities in Tasmania. The analysis gave the following results:—

SiO <sub>2</sub> .	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Na <sub>2</sub> O + K <sub>2</sub> O.	Total.
62.41	24.62	11.26	0.14	1.40	0.43	100.26

B. H. B.

**Wollastonite from Rézbánya.** By J. LOCZKA (*Zeit. Kryst. Min.*, **10**, 89).—The analysis gave the following results:—

SiO <sub>2</sub> .	CaO.	MgO.	FeO.	MnO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.
51·61	46·29	1·08	0·51	0·47	0·13	0·11	0·54
	Al <sub>2</sub> O <sub>3</sub> .	Total.					
	trace	100·74			Density.		
					2·919		

B. H. B.

**The Augites of the Kaiserstuhl Mountains in Baden.** By A. KNOP (*Zeit. Kryst. Min.*, **10**, 58—81).—The augites of the Kaiserstuhl are of great interest mineralogically and petrographically. The author classes them into four types:—1. Augites which appear as characteristic constituents of basalt. They are of a black colour, and usually exhibit the combination  $\infty P\infty$ ,  $\infty P$ , +  $P$ ,  $\infty P\infty$ . In thin sections, they are transparent and of a brownish-violet colour. The extinction angle is 45°. 2. Augites which occur as an essential constituent of phonolites. These occur but rarely as well-developed crystals. They are of a coal-black colour; but under the microscope they appear green and transparent. 3. Augites which occur in limestone. After dissolving the granular limestone of certain portions of the Kaiserstuhl mountains in hydrochloric acid, grains of greenish-yellow augite remain. Under the microscope they are very transparent and of a pale yellowish-green colour. 4. Augites in basalt. Grains of a transparent green augite resembling diopside are occasionally found in the basaltic rock, containing hyalosiderite, from Thüringen, in the limburgite near Limburg, and in the basalt of the Lützelberg (see Analysis 6).

The author gives the following analyses of these augites:—Group I. Augites which are of a brownish-violet colour when seen in thin sections or as powder: 1. From the so-called limburgite; 2. From the porphyritic basalt of Burkheim; 3. From the hauyn-basalt of Oberbergen; 4. From the porphyritic basalt of Amoltern.

	1.	2.	3.	4.
SiO <sub>2</sub> .....	44·15	45·83	46·54	47·20
TiO <sub>2</sub> .....	4·57	3·57	2·85	2·70
Al <sub>2</sub> O <sub>3</sub> .....	6·90	7·47	8·20	5·80
Fe <sub>2</sub> O <sub>3</sub> .....	6·02	4·90	3·72	3·17
FeO .....	3·49	4·11	4·32	4·76
MgO .....	12·28	10·92	13·19	12·79
CaO .....	22·79	22·83	21·29	23·02
Totals .....	100·20	99·63	100·11	99·44

Group II. Augites which are of a green colour when seen in thin sections or as powder; 5. Augite from the phonolite of Oberschaffhausen; 6. Augite enclosed in the basalt of the Lützelberg; 7. Yellowish-green augites from the limestone of Badloch.

	5.	6.	7.
SiO <sub>2</sub> .....	49·75	51·37	52·09
TiO <sub>2</sub> .....	1·45	0·94	0·95
Al <sub>2</sub> O <sub>3</sub> .....	0·53	2·43	1·18
Fe <sub>2</sub> O <sub>3</sub> .....	13·23	4·14	1·59
FeO.....	9·66	4·46	1·57
MnO .....	1·09	trace	trace
MgO .....	4·55	13·55	18·10
CaO.....	16·72	22·72	23·56
K <sub>2</sub> O.....	0·00	0·61	0·48
Na <sub>2</sub> O .....	2·26	0·44	0·48
Totals.....	99·24	100·66	100·00

B. H. B.

**Augites of Noteworthy Composition.** By C. DÖLTER (*Zeit. Kryst. Min.*, 10, 106—108).—The author gives the composition of the following augites:—1. Augite from the nepheline basalt of Rib. das Patas; 2. Augite from the Island of S. Antão; 3. Augite crystal from the Garza Valley; 4. Augite crystal from Aguas das Caldeiras; 5. Augite from the dolerite of St. Vincente; 6. Augite from Siderao; 7. Augite from the phonolite of Praya; 8. Augite from the tephrite of the Pico da Cruz.

B. H. B.

**Analyses of Transylvanian Minerals.** By F. KOCH (*Zeit. Kryst. Min.*, 10, 99—100).—1. The analysis of the so-called *szaboite* from the Aranyer Mountain gave the following results:—

SiO <sub>2</sub> .	MgO.	FeO.	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	Ignition.	Total.
51·681	22·824	8·465	12·687	3·093	0·960	99·710

The material employed was weathered. An analysis of perfectly fresh material gave 19·702 per cent. of FeO. The author concludes that this so-called *szaboite* from the Aranyer Mountain is a true hypersthene. The same conclusion was arrived at by Krenner (*Zeit. Kryst. Min.*, 9, 255) from a crystallographical examination of the mineral in question.

2. Two specimens of *celestine*, from Bács, were analysed: I. A bluish-grey translucent celestine, which filled the interior of an *Echinolampas giganteus*; II. Tabular translucent grey crystals from calcareous marl. The results were as follows:—

	SO <sub>3</sub> .	SrO.	CaO.	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	Ignition.	Total.
I.	43·370	54·586	0·752	0·431	0·447	0·371	99·957
II.	43·428	54·450	1·090	0·484	0·140	0·334	99·926

B. H. B.

**Andesite from Trifail in Styria.** By R. MALY (*Monatsh. Chem.*, 6, 75—76).—The remarkable occurrence of this mineral in brown coal has been described by J. Rumpf. On analysis it gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.
57·53	26·62	8·48	0·23	6·90	0·39 = 100·15

Oxygen ratio: MO : M<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> = 1·00 : 2·85 : 7·03.

H. B.

### Analysis of Sericite from the Quartz-phyllite of Wiltau.

By C. SENHOFER (*Zeit. Kryst. Min.*, **10**, 105).—The analysis gave the following results:—

[illegible]

## Organic Chemistry.

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**Reduction of Cetyl Iodide with Sodium Amalgam.** By LEBEDEF (J. Russ. Chem. Soc., 1884 [2], 299—300).—Cetyl iodide, obtained by the direct action of phosphorus tri-iodide on the alcohol, was treated with sodium amalgam. After a time, a crystalline hydrocarbon separated, melting at  $70.5^{\circ}$ ; this is called dotriakontene,  $C_{32}H_{66}$ . On evaporation, the filtrate left so small a quantity of an impure product, that it was impossible to decide if  $C_{16}H_{34}$  was formed in the reaction, as was expected by the author. A. T.

**Trimethylene Iodide.** By L. HENRY (Ber., 18, 519—521).—The author refers to Perkin's method of preparing this substance (this vol., p. 495) as being the method by which he had himself prepared trimethylene iodide. He has also shown that the iodhydrins may be obtained from sodium iodide and the brom- or chlor-hydrins, and likewise by the same method, propargyl iodide (Abstr., 1884, 979). Trimethylene iodide boils at  $224^{\circ}$  (pressure 763 mm.); it remains liquid at  $-20^{\circ}$ . A difference in physical properties, similar to that between trimethylene and ethylene iodides (m. p.  $82^{\circ}$ ), is shown to exist in other corresponding derivatives of the two series. A. K. M.

**Action of Chlorine on Trimethylethylene.** By T. KONDAKOFF (J. Russ. Chem. Soc., 1885, 144—145).—Pure trimethylethylene prepared from tertiary amyl iodide was treated with chlorine, when considerable quantities of hydrogen chloride were evolved, and chiefly, although not exclusively, unsaturated chlorinated compounds were formed, boiling at  $80-110^{\circ}$ , and consisting of  $C_5H_9Cl$ ,  $C_5H_{11}Cl$ , and  $C_5H_{10}Cl_2$ . On treating the portion boiling below  $100^{\circ}$  with water, the author obtained along with some quantity of tertiary amyl alcohol a new unsaturated secondary alcohol, boiling at  $115-117^{\circ}$ . It takes up bromine, forms alcoholates with sodium and barium, and is considered to be methyl isopropenyl carbinol. By the action of dilute sulphuric acid, the alcohol undergoes isomeric change into methyl isopropyl ketone. A. T.

**Isomerism of Acetylene Hydrocarbons.** By A. FAVORSKY (J. Russ. Chem. Soc., 1885 [1], 143—144).—The author studied the reaction of dry and of alcoholic potassium hydroxide with the pro-

ducts of the action of phosphorus pentachloride on methyl ethyl ketone and methyl propyl ketone. On using the hydroxide in the dry state, ethylacetylene and propylacetylene are formed, giving characteristic precipitates with ammoniacal solutions of cuprous chloride and silver nitrate; whilst alcoholic potash, on the other hand, yields dimethylacetylene and methylethylacetylene, the former giving, on shaking with sulphuric acid, crystalline hexamethylbenzene, the latter identified by its boiling point. In both reactions, monosubstituted acetylene is first formed, but on further heating with excess of the alcoholic alkali solution, undergoes isomeric change into a bisubstituted compound. This was proved by heating ethylacetylene and propylacetylene in sealed tubes at  $170-180^{\circ}$ , when hydrocarbons were formed, which did not give metallic derivatives. The isomeric conversion is due to the alcoholic alkali solution, as neither dry potassium hydroxide nor alcohol produces this effect. A. T.

**Preparation of Chromium and Manganese Compounds, analogous to Ferro- and Ferri-cyanide of Potassium.** By O. T. CHRISTENSEN (*J. pr. Chem.* [2], 31, 163—173).—*Potassium Chromicyanide*,  $K_6Cr_2Cy_{12}$ .—This salt is best prepared as follows:—Freshly precipitated moist chromic hydroxide is dissolved in acetic acid, evaporated nearly to dryness, and diluted to 250 c.c. with water: this solution is gradually added to almost boiling potassium cyanide (200 grams potassium cyanide + 600 to 700 c.c. water) contained in a flask, so as to exclude the carbonic anhydride of the air; after heating for a short time, the liquid is filtered, evaporated, and cooled. The crystals obtained are dissolved in water (4 parts), and the solution boiled, the deposited chromic hydroxide is filtered off, and the solution when cooled yields pale yellow crystals, more of which are obtained by repeatedly boiling the mother-liquor. The salt has been described by Kaiser (*Annalen*, Suppl., 3, 170).

*Potassium Manganicyanide*,  $K_6Mn_2Cy_{12}$ .—Eaton and Fittig obtained this compound by the oxidation of potassium manganocyanide. It is, however, more readily prepared by adding manganic acetate or phosphate (described by the author, *Abstr.*, 1884, 398) to a solution of potassium cyanide; the solution becomes yellow, and then deep brown; on filtering and cooling, red-brown needles of potassium manganicyanide separate out. On dissolving the salt in a hot solution of potassium cyanide, reduction takes place, and the solution becomes yellow; on adding water and again heating, the red colour reappears, manganic hydrate separates, and the cooled solution deposits crystals of potassium manganicyanide.

*Potassium Chromocyanide*,  $K_4CrCy_6 + 3H_2O$ .—Descamps has obtained the pure salt. Moissan prepared a salt called by him potassium chromocyanide, but owing to its colour and properties, the author believes it to be the chromicyanide. Chromous acetate was shaken up with carbonic acid water, then poured into a 25 per cent. solution of potassium cyanide, and the whole gently warmed in a flask through which a stream of hydrogen was passed; the vessel was then surrounded with snow, and potassium cyanide added to the liquid; a dark blue crystalline precipitate was thrown down. This precipitate corre-

sponds exactly with the potassium chromocyanide described by Descamps. As no oxidation occurred during the preparation, it is evident that Moissan's salt must have been the chromi-compound.

*Potassium Manganocyanide*,  $K_4MnCy_6 + 3H_2O$ .—Eaton and Fittig and Descamps have given good methods for the preparation of this salt; the following method is more speedy:—10 grams of manganous acetate are added to an almost boiling solution of 40 to 45 grams potassium cyanide in 100 c.c. of water; a green compound forms, which redissolves on addition of 15 to 20 grams of potassium cyanide, and at the same time a fine crystalline dark blue precipitate of potassium manganocyanide separates. Potassium cyanide dissolves this precipitate with difficulty; on diluting with water, it dissolves, and on filtering and cooling, large dark blue crystals are formed.  
H. P. W.

**Potassium Chromocyanide.** By H. MOISSAN (*Ann. Chim. Phys.* [6], 4, 136—144).—*Potassium chromocyanide*,  $K_4CrCy_6$ , is best prepared by the action of potassium cyanide on chromous carbonate; the latter salt is obtained by acting on a solution of chromous chloride saturated with carbonic anhydride, with a solution of potassium carbonate, air being excluded; the greyish-white precipitate is mixed with a solution of potassium cyanide, when the precipitate partially dissolves, the liquid becoming yellow, and from this solution after filtration the yellow crystals of potassium chromocyanide may be obtained by evaporation; it has a sp. gr. of 1.71. 10 c.c. of water at 20° dissolve 3.233 grams of this salt; it is precipitated from its aqueous solution by alcohol, in which it is completely insoluble, as it is also in ether, benzene, and chloroform. Its aqueous solution when examined with a spectroscope shows complete absorption in the violet end, and three well-marked bands in the green. The salt is anhydrous, and is unchanged by exposure to the air at ordinary temperatures. The taste is similar to that of the ferrocyanide; its aqueous solution gives a feebly alkaline reaction, and on boiling a slight odour of hydrocyanic acid is perceived, chromous hydroxide being precipitated. On electrolysis, potassium chromicyanide is formed at the positive pole, whilst hydrogen and potassium hydroxide are disengaged at the negative. Heated to low redness in the absence of air, the salt melts and gives off nitrogen, a residue of chromium more or less carburised and of potassium cyanide remaining. Heated with concentrated or dilute sulphuric acid, it behaves like the corresponding ferrocyanide; oxidising agents convert it into chromicyanide. It gives precipitates with solutions of a considerable number of the metallic salts. The most characteristic reaction, however, is the red coloration formed on the addition of ferrous sulphate, a distinct coloration being obtained with a solution containing only  $\frac{1}{10000}$  part of the chromocyanide. Potassium chromocyanide is not poisonous even when administered by hypodermic injection.

*Chromocyanic acid* is obtained in small white crystals by the decomposition of the potassium salt with dilute sulphuric acid; it is soluble in water, but the solution is not stable, decomposing rapidly in air. The aqueous solution of the acid decomposes carbonates.

A. P.

**Formation of Nitroprussides without the Use of Nitric Acid.** By H. O. JENSEN (*J. Pharm.* [5], **11**, 315—318).—These compounds are usually produced by Playfair's method, in which potassium ferro- or ferri-cyanide is treated with nitric acid. The author finds, however, that they can be produced without the aid of nitric acid. If an electric current from two Bunsen cells be passed for some time through a solution of potassium ferrocyanide, the solution becomes brown and alkaline and gives a strong nitroprusside reaction with ammonium sulphide. The reaction probably commences, as has been indicated by Daniell, Miller, and others, by the formation of ferricyanide at the positive pole, and the transference of caustic potash to the negative. On placing the electrodes in separate tubes, connected by an inverted syphon of small bore, and employing three cells, no trace of nitroprusside could be detected in the solution, the reaction of which was acid at the positive and alkaline at the negative pole. Powdered potassium ferricyanide was treated gradually with calcium hypochlorite solution; an active reaction took place. At 70° to 80° much gas was disengaged, in which carbonic anhydride was present, and a reddish-brown deposit was formed. A dried sample of this brown deposit gave 19 per cent. of ferric oxide, and 78·80 per cent. of calcium carbonate. The solution was concentrated by evaporation, cooled and treated with alcohol to extract the nitroprusside. After removing the alcohol by distillation the nitroprusside was precipitated by cupric chloride. The copper salt is subsequently decomposed by means of sodium hydroxide solution. The sodium salt can be purified by dissolving in a little water, adding strong alcohol, filtering, and crystallising. J. T.

**Polymeric Dichloroacetonitriles.** By A. WEDDIGE and M. KÖRNER (*J. pr. Chem.* [2], **31**, 176).—When hydrogen chloride is passed into ordinary dichloroacetonitrile, a white, crystalline, easily decomposable compound is formed, which, when heated for several hours at 130—140° in a sealed tube, splits up into hydrogen chloride and a polymeric modification of dichloroacetonitrile, which crystallises in rather large prisms melting at 69—70°; it is easily soluble in alcohol, ether, and benzene, but only sparingly in water; it does not possess basic properties, and it is not changed by alkalis or ammonia in the cold. Hydrochloric acid also forms additive products with mono- and tri-chloroacetonitrile, but only the latter yields a polymeric modification, which is identical with the nitrile obtained from ethyl paracyanocarbonate. H. P. W.

**Preparation of Cyanamide.** By J. TRAUBE (*Ber.*, **18**, 461—463).—It has been recently shown that in preparing cyanamide from *pure* thiocarbamide melting at 169°, the desulphuration of the latter is incomplete, even after several days. The author prepared thiocarbamide from ammonium thiocyanate, and found that the first crystallisations melting at about 149° were readily desulphurised by freshly precipitated mercuric oxide, whilst the pure compound was only partially converted after several days. The ready conversion of the impure substance is found to be due to the presence of ammonium



thiocyanate, as when some of this is added to the pure thiocarbamide the mixture is readily convertible into cyanamide. Dimercurammonium chloride produces the same effect as mercuric oxide, the products of the reaction being mercuric sulphide, cyanamide, ammonium chloride, and free ammonia.

Instead of preparing cyanamide by passing cyanogen chloride into a solution of dry ammonia in absolute ether, a better result is obtained by employing aqueous ammonia. The cyanamide is then converted into the lead or silver compound, and the latter decomposed by hydrogen sulphide. This method is, however, much less to be recommended than that mentioned above. A. K. M.

**Unsaturated Compounds of the Fatty Series.** By F. BEILSTEIN and E. WIEGAND (*Ber.*, **18**, 481—483).—*Allyl alcohol*,



was treated with dehydrating agents in the hopes of obtaining symmetrical allylene,  $\text{CH}_2 : \text{C} : \text{CH}_2$ . With phosphoric anhydride, a very violent reaction takes place, but without production of allylene; with concentrated sulphuric acid, total carbonisation occurred, whilst with dilute acid, condensation-products appear to be formed; in no case was allylene obtained.

*Methenyltriallyl Ether*,  $\text{CH}(\text{OC}_3\text{H}_5)_3$ .—In order to obtain this compound, sodium (16 grams) is gradually added to a mixture of allyl alcohol (35 grams), and chloroform (24 grams), diluted with twice its volume of light petroleum. The whole is warmed, the solution filtered from the sodium chloride and distilled. Methenyltriallyl ether is a liquid boiling at  $196-205^\circ$ . When allyl alcohol (20 grams) is heated with chloroform (55 grams), potash (140 grams), and water (200 grams), a vigorous reaction takes place with evolution of carbon monoxide and production of formic acid. No methenyltriallyl ether is formed.

*Crotonic acid* was prepared by distilling  $\beta$ -hydroxybutyric acid, this being obtained by the action of sodium-amalgam (in much larger proportion than recommended by Wislicenus, *Annalen*, **149**, 208) on ethyl acetoacetate; the alkaline solution is acidulated with sulphuric acid, distilled, and the crotonic acid extracted with ether. The author has prepared salts, the properties of which however do not agree with Claus's descriptions (*Annalen*, **131**, 63); the calcium salt,  $(\text{C}_4\text{H}_5\text{O}_2)_2\text{Ca}$ , and barium salt,  $(\text{C}_4\text{H}_5\text{O}_2)_2\text{Ba}$ , are described. Attempts to prepare crotonamide by heating ammonium crotonate, by treating crotonic chloride with ammonia, and by heating ethyl crotonate with concentrated aqueous ammonia at  $100-150^\circ$ , yielded in all cases a syrup moderately soluble in water, whilst according to Pinner (*Abstr.*, 1884, 1292) it is a crystalline substance melting at  $149-152^\circ$ .

Salts of *sulphobutyric acid*,  $\text{C}_4\text{H}_5\text{SO}_3$ , are prepared by heating crotonic acid with an aqueous solution of ammonium or potassium sulphite at  $130^\circ$ . The barium salt,  $\text{C}_4\text{H}_5\text{SO}_3\text{Ba} + 2\text{H}_2\text{O}$ , and lead salt,  $\text{C}_4\text{H}_5\text{SO}_3\text{Pb}$ , are described.

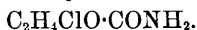
Tiglic and angelic acids also combine readily with alkaline sulphites at an elevated temperature. A. K. M.

**Action of Dilute Acids on Allyl Alcohol.** By V. SOLONINA (*J. Russ. Chem. Soc.*, 1885 [1], 145—146).—On treating allyl alcohol at 100° with dilute sulphuric or hydrochloric acid, an unsaturated aldehyde,  $C_6H_{10}O$ , boiling at 135—138°, is obtained, probably the same as that prepared by Lieben by condensation of propaldehyde. It is suggested that the formation of the compound may be due to previous isomeric change of allyl alcohol into propaldehyde. From the products of the action of hydrochloric acid on allyl alcohol, allyl chloride and allyl ether were isolated. A. T.

**Diallyl Dioxide.** By S. PRZYBYTEK (*J. Russ. Chem. Soc.*, 1885 [1], 136—141).—By the action of dry potassium hydroxide on the dichlorohydrol  $C_6H_{10}(OH)_2Cl_2$ , obtained by the addition of hypochlorous acid to diallyl, a dioxide of the composition  $C_6H_{10}O_2$  is formed, which could not be separated from the product in a state of purity, as it obstinately retains an admixture of some volatile chlorinated compound. On heating the dioxide with water in presence of baryta, a syrupy substance was obtained easily soluble in water, almost insoluble in ether; this proved to be the first anhydride of hexyl erythrol. It takes up water with difficulty, being partly converted into the tetrahydric alcohol itself. By the action of dehydrating agents on the anhydride, the author succeeded in preparing diallyl dioxide in a pure state, and in undertaking its analysis and the determination of its vapour-density. He intends to study the modes of formation of this, as well as of other analogous dioxides. A. T.

**Action of Carbonyl Chloride on Glycol Chlorhydrin.** By J. NEMIROWSKY (*J. pr. Chem.* [2], 31, 173—175).—A continuation of the author's researches (*Abstr.*, 1884, 419). When liquid carbonyl chloride acts on ethylene chlorhydrin, it forms, not as was expected, chlorethyl carbonate,  $C_2H_4Cl \cdot O \cdot CO \cdot O \cdot C_2H_4Cl$ , but *chlorethyl chloroformate*,  $ClCO \cdot OC_2H_4Cl$ .

It is a clear fuming liquid, insoluble in water, but readily soluble in alcohol and ether, and boils between 150—160°. It is not decomposed by boiling with water, but continued heating with dilute aqueous potash converts it into glycol and potassium carbonate and chloride. When heated with ammonia, it yields *chlorethyl carbamate*,



This crystallises in large prisms, melts at 76°, and is easily soluble in water, alcohol, and ether. In a similar manner the corresponding chlorethyl carbanilate,  $C_2H_4ClO \cdot CO \cdot NHPh$ , was obtained. It crystallises in needles, melts at 51°, and is soluble in alcohol and ether, insoluble in cold, sparingly soluble in hot water. When boiled for a short time alone, and then with strong aqueous potash, a substance of the formula  $C_9H_9NO_2$  is obtained; it forms white rhombic tabular crystals, melts at 124°, and when heated at 170° with strong hydrochloric acid yields *chlorethyl phenylamine hydrochloride*,  $NHPh \cdot C_2H_4Cl \cdot HCl$ , which crystallises in large monoclinic prisms melting at 158°; when treated with potash, an oil (probably the free base) is precipitated; it is soluble in ether, and volatilises in steam, with partial conversion into a solid white modification.

H. P. W.

**Elementary Composition of Nitroglycerol.** By M. HAY and O. MASSON (*Proc. Roy. Soc. Edin.*, **32**, 87—91).—After reference to former work on nitroglycerol by Williamson and others, the authors detail their process for preparing the compound. One part by weight of pure glycerol was added drop by drop to 2 parts nitric acid (1.49) and 6 parts sulphuric acid (sp. gr. 1.84), the two being kept below 10°. After ten minutes the mixture was thrown into water, and the precipitated oil was well washed and dried at 60—80°, finally being kept in a vacuum for twelve days over sulphuric acid, sp. gr. at 14.5° = 1.601. The combustion was made by weighing out 0.2 = 0.4 gram into a porcelain boat containing fine copper oxide, and then adding another layer of the oxide. After the boat had been introduced into the combustion tube, its contents were thoroughly mixed with the oxide in the tube, then the combustion was proceeded with in the ordinary way. Nitrogen determinations were 18.25 and 18.06 (theory 18.5). Difference in preparation does not cause a difference in composition. From these results and those obtained by Hay (next Abstract) the authors conclude that the generally accepted constitution of trinitroglycerol is correct. E. W. P.

**Chemistry of Nitroglycerol.** By M. HAY (*Trans. Roy. Soc. Edin.*, **32**, 67—86).—From the resemblance of nitroglycerol to the nitrites in its physiological and therapeutical properties, the author was at first inclined to regard it as being a glyceryl nitrite instead of a nitrate, but the result of a further investigation did not confirm this view. Railton and others have stated that nitroglycerol when treated with alcoholic potash yields glycerol and potassium nitrate. This statement is quite incorrect; the decomposition is of a complex nature. No glycerol is obtained, as it is oxidised at the expense of the NO<sub>3</sub> groups, about two-thirds of which suffer reduction to the nitrous condition, only about one-third being found as nitrate at the end of the reaction. The other products of the reaction are potassium acetate, oxalate, and formate, a small amount of ammonia, and a reddish-brown resinous substance, which gives a dark colour to the liquid. Numerous determinations of the amount of nitrite formed showed that 100 parts of nitroglycerol gave from 34.14 to 35.24 parts of nitrous anhydride. (If two-thirds of the nitrogen were converted into nitrous anhydride the amount would be 33.48.) As it was also found that 5 mols. of potash were required to decompose 1 mol. of nitroglycerol, it seems that the principal reaction may be expressed by the equation  $C_3H_5(O\cdot NO_2)_3 + 5KOH = KNO_3 + 2KNO_2 + CH_3\cdot COOK + H\cdot COOK + 3H_2O$ . The reaction is the same either with alcoholic or aqueous potash, but is very slow in the latter case, owing to the sparing solubility of nitroglycerol in water.

Ammonia and alkaline carbonates act in a manner similar to potash. The same may be said for sodium hydrogen phosphate, but the reaction is much less powerful, whilst sodium chloride exerts hardly any action. Hydrochloric acid acts less powerfully than alkaline carbonates, and sulphuric acid (1 : 10) less powerfully still, whilst the concentrated acid has no action. De Vrij's statement that nitroglycerol is decomposed by sulphuretted hydrogen, is not correct. The

alkaline sulphides decompose nitroglycerol, sulphur being precipitated, and the reaction is rapid, and seems to be promoted by the sulphur, yet the particular part played by that element has not been ascertained. Hot water decomposes nitroglycerol slowly. The amount of nitroglycerol formed from a given weight of glycerol agrees fairly with the assumption of its being glyceryl trinitrate.

As different statements have been made as to the physical characters of nitroglycerol, the author has prepared it in a state of purity, and finds that it is perfectly colourless, and remains so even when exposed to air. It keeps equally well in water or alcohol. Heated on the water-bath no change occurs, unless acids or alkalis are present.

1 gram of nitroglycerol dissolves in 800 c.c. water; in 3 c.c. alcohol; in 10.5 c.c. alcohol (sp. gr. 0.846); in 1 c.c. methyl alcohol (sp. gr. 0.814); in 4 c.c. methylated spirit (sp. gr. 0.830); in 18 c.c. amyl alcohol; in less than 1 c.c. benzene; in 120 c.c. carbon bisulphide; in all proportions in ether, chloroform, glacial acetic acid, and phenol; and sparingly in glycerol.

Nitroglycerol can be estimated with tolerable accuracy by determining the amount of nitrite formed by boiling with alcoholic potash, and assuming that 100 parts of nitroglycerol yield 33.48 parts of nitrous anhydride.

E. W. P.

**Mannitol Lead Nitrate.** By A. SMOLKA (*Monatsh. Chem.*, 6, 198—203).—When ammonia is added to an aqueous solution containing lead nitrate and mannitol in the proportion of 2 mols. of the former to not less than 1 mol. of the latter, a compound is precipitated which has the composition  $C_6H_8O_6Pb_4(NO_3)_2$ . This substance is sparingly soluble in water and insoluble in alcohol. It detonates when suddenly heated. The nitric acid in the compound is not eliminated by treatment with ammonia.

W. C. W.

**Reduction of Mannitol by Formic Acid.** By A. FAUCONNIER (*Compt. rend.*, 100, 914—915).—When mannitol is heated for eight hours with  $2\frac{1}{2}$  times its weight of formic acid of about 80 per cent., and the product is distilled at  $100^\circ$ , a brownish viscous substance is obtained, which solidifies to a crystalline mass on cooling. This product consists of a mixture of the mono- and di-formic ethers of mannitol, or rather of mannitan. If mannitan is substituted for mannitol in this operation, the same products are obtained. When the mixture of ethers is subjected to destructive distillation it begins to decompose at about  $210^\circ$ , with evolution of carbonic oxide and carbonic anhydride, whilst a yellowish liquid distils over, which can be separated by fractionation into three products, namely, isomannide,  $C_6H_{10}O_4$ ; a colourless viscous liquid, which boils at  $157^\circ$  under a pressure of 17 mm., and seems to have the composition  $C_6H_{10}O_3$ ; and a colourless liquid which boils at  $107$ — $109^\circ$  under ordinary pressure. This last liquid has the composition  $C_6H_8O$ , is almost insoluble in water, but dissolves in alcohol, chloroform, ether, and carbon bisulphide, and has an odour resembling that of carbylamines and oil of mustard; sp. gr. at  $0^\circ$  compared with water at  $4^\circ = 0.9396$ ; levorotatory power for  $[\alpha]_D = -168^\circ 24'$ . The action of the formic acid

seems to result in the dehydration of mannitol with formation of mannitan, the etherification of mannitan with subsequent decomposition of the ethers, and also dehydration of the mannitan, the latter change yielding isomannide. C. H. B.

**Anhydrides of Mannitol.** By A. ALEKHINE (*J. Russ. Chem. Soc.* 1884 [2], 249).—The so-called uncrystallisable mannitan is a mixture of diverse dehydration products of mannitol, as the author has succeeded in separating from it under diminished pressure, without any symptom of decomposition, Fauconnier's isomannide and other anhydrides of mannitol. A. T.

**Nomenclature of Sugars.** By C. SCHEIBLER (*Ber.*, 18, 606—648).

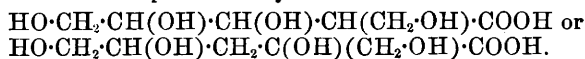
**Isosaccharin.** By H. KILIANI (*Ber.*, 18, 631—641).—In continuation of his researches on saccharin (*Abstr.*, 1883, 565, 962), the author now endeavours to ascertain the constitution of isosaccharin—a substance originally obtained by Cuisinier (*Monit. Sci.*, 1882, 521) from the maltic (isosaccharic) acid obtained by Dubrunfaut by the action of lime-water on maltose (*ibid.*, 520).

Isosaccharin is readily prepared by dissolving 1 kilo. of commercial milk-sugar in 9 litres of water, adding 450 grams of calcium hydroxide, and allowing the mixture to remain, with frequent shaking, for six weeks. The reaction is much accelerated by heating, but the yield is then considerably diminished. The filtered liquid is saturated with carbonic anhydride, heated to boiling, filtered, and the filtrate evaporated to about 2 litres; during the evaporation a considerable portion of the sparingly soluble calcium isosaccharate separates, the remainder crystallises out after 24 hours. The calcium salt is decomposed with oxalic acid, and the filtered liquid evaporated to a thin syrup, which on cooling solidifies to a crystalline mass of impure isosaccharin; this is purified by washing with absolute alcohol.

When isosaccharin is reduced with hydriodic acid and amorphous phosphorus, if the reaction is pushed as far as possible, it yields methylpropylacetic acid, as already shown by the author to be the case with saccharin; if the reduction is less energetic, then there were obtained  $\alpha$ -methylvalerolactone, a solid white substance of the formula  $C_{10}H_{18}O_2$ , insoluble in the ordinary solvents, and a crystalline lactone,  $C_8H_{10}O_2$ , melting at  $137^\circ$  and readily sublimable; when boiled with baryta-water, this lactone yields a barium salt,  $(C_6H_{11}O_3)_2Ba$ , crystallising in lustrous needles.

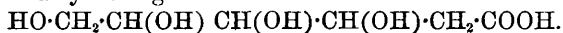
When isosaccharic acid is oxidised with silver oxide, it yields carbonic anhydride, oxalic and glycollic acids, but, unlike saccharin, it does not yield acetic acid; it therefore does not contain a methyl-group. When oxidised with nitric acid, it yields glycollic and *dihydroxypropenyltricarboxylic acid*. This latter acid,  $C_3H_3(OH)_2(COOH)_3$ , forms a colourless syrup; it is very unstable, suffering partial decomposition, with elimination of carbonic anhydride at  $100^\circ$ . The normal calcium, barium, strontium, and lead salts are very sparingly soluble in water and difficult to crystallise. The hydrogen calcium salt,

$(C_6H_7O_8)_2Ca$ , crystallises readily in small lustrous prisms. When heated with hydriodic acid and amorphous phosphorus, the free acid is converted into glutaric acid. From these results, it follows that isosaccharin must be represented by one of the two formulæ



A. J. G.

**Metasaccharin.** By H. KILIANI (*Ber.*, 18, 642—645).—The preparation of metasaccharin from the mother-liquors from calcium isosaccharate has been already described by the author (*Abstr.*, 1884, 283). When metasaccharin is reduced by hydriodic acid and amorphous phosphorus, it yields normal caprolactone, showing that, unlike its isomerides, it must have a normal constitution. When oxidised by nitric acid, metasaccharin is converted into *trioxyadipic acid*,  $C_4O_5(OH)_3(COOH)_2$ ; this crystallises in colourless monoclinic tables, melts at  $146^\circ$  with decomposition, and is soluble in water, sparingly soluble in ether and alcohol. The calcium salt crystallises in stellate groups of microscopic needles. The free acid is converted into adipic acid when reduced. The author regards metasaccharic acid as probably having the constitution



A. J. G.

#### Decomposition of Sugar when Heated with Dilute Acids.

By M. CONRAD and M. GUTHZEIT (*Ber.*, 18, 439—444).—In this paper the authors describe quantitative experiments on the action of dilute sulphuric and hydrochloric acids of known strength on weighed quantities of cane-sugar. After 15 to 20 hours' boiling, the solution was filtered cold from the humin compounds, and the residue was extracted with boiling water until the washings cease to be acid. The united filtrates are made up to a definite volume. One portion of this was examined for total acidity, another was distilled with steam, and the proportion of volatile (formic acid) to non-volatile acid (acetopropionic acid) determined, whilst in a third portion the amount of unaltered dextrose was estimated. The results are tabulated as follows:—

#### *Decomposition of Dilute Sulphuric Acid.*

	Ingredients in grams.			Decomposition products per 100 parts sugar.			
	Sugar.	Water.	$H_2SO_4$ .	Humin substances.	Dextrose.	Acetopropionic acid.	Formic acid.
1	150	150	9.48	16.7	41.7	15.9	7.7
2	20	25	1.78	16.6	47.2	16.6	7.9
3	20	20	1.76	17.5	38.5	17.0	8.0
4	50	150	9.48	19.4	36.4	17.3	8.4
5	20	50	3.57	13.0	53.0	20.1	8.8

*Decomposition by Dilute Hydrochloric Acid.*

	Sugar.	Water.	HCl.	Humin substances.	Dextrose.	Acetopropionic acid.	Formic acid.
1	150	390	37.5	15.8	30.4	27.9	8.7
2	20	60	4.49	18.2	22.7	31.0	13.8
3	20	50	5.11	19.0	21.5	33.6	14.2
4	20	60	4.49	19.5	17.7	35.0	13.5
5	20	50	9.43	27.0	—	37.8	14.9

It will be seen that in the second series of experiments a much larger proportion of acetopropionic acid is produced than in those in which sulphuric acid was employed, and that the amount of humin substance increases with the acetopropionic acid. In the first table, the average proportion of acetopropionic to formic acid is as 116 : 54, whilst in the second table the proportion is as 116 : 46, which is that required by the equation  $C_{12}H_{22}O_{11} = 2C_6H_8O_3 + 2CH_2O_2 + H_2O$ .

Analyses of the humin substance obtained by the action of sulphuric acid on sugar, yielded numbers corresponding with the formula  $C_{24}H_{18}O_6$ , whilst the substance obtained from hydrochloric acid and sugar corresponded with  $C_{49}H_{34}O_{17}$ .

A. K. M.

**Remarks on some Criticisms of Friedel's concerning Chloral Hydrate.** By L. TROOST (*Compt. rend.*, 100, 834—837).

**Reply to Remarks by Troost concerning Chloral Hydrate.** By FRIEDEL (*Compt. rend.*, 100, 891—892).

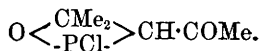
**Reaction of Acetone with Amides of the Acetic Series.** By F. CANZONERI and G. SPICA (*Gazzetta*, 14, 341—351).—On heating acetone with acetamide and zinc chloride in closed tubes there is formed, as the principal product of the reaction, a basic substance of composition  $C_9H_{15}N$ . This compound agrees in its chemical and physical characteristics with the dehydrotriacetonamine found by Heintz among the basic substances formed by the action of ammonia on acetone. In the synthesis effected by the author, it is probably derived from acetanamine by the abstraction of a molecule of water,  $C \ll \begin{smallmatrix} CH \cdot CMe_2 \\ CH \cdot CMe_2 \end{smallmatrix} > NH$ . As a subsidiary product of the above reaction an alkaloid is produced boiling about  $240^\circ$ ; its composition is probably expressed by the formula  $C_{18}H_{23}N = C_3H_{15}N + 2C_3H_6O - 2H_2O$ ; its platinumchloride crystallises in red dodecahedra. If the explanation of the mechanism of the above reaction be correct, then, even if formamide be substituted for acetamide, the product formed should be the same. This was confirmed. When acetamide and acetone are heated with zinc chloride at temperatures above  $400^\circ$ , a series of basic compounds are probably formed, derived from 1 mol. of the

base  $C_9H_{15}N$ , and 2, 3, or 4 mols. of acetone with abstraction of the same number of molecular proportions of water.

If mesityl oxide is heated with equal molecular proportions of acetamide in the presence of an excess of zinc chloride, a basic substance is produced of the composition  $C_8H_{13}NO$ , a yellowish liquid boiling between  $175-180^\circ$ . It is proposed to call this substance oxyhydrocollidine; its composition is identical with that of the pelletierine obtained by Tanret from pomegranate (Abstr., 1879, 170).

*Note.*—The base pelletierine, as described in the Abstract referred to above, has the composition  $C_{16}H_{13}NO_2$ . V. H. V.

**Acetone Phosphorus Compounds.** By A. MICHAELIS (*Ber.*, 18, 898—910).—In a former communication (Abstr., 1884, 991) the author described the compound  $C_6H_{10}O_2PCl$ , obtained by the action of aluminium chloride on a mixture of acetone and phosphorous chloride, which he now styles *diacetone phosphorus chloride*,



It forms a colourless crystalline mass, consisting of strongly doubly-refractive crystals belonging to the tri- or mono-clinic systems; it melts at  $35-36^\circ$ , forming a liquid of a sp. gr. 1.209 at  $17.5^\circ$ . It boils at  $235^\circ$  under a pressure of 745 mm. and at  $154^\circ$  under a pressure of 100 mm. Water decomposes this chloride, forming diacetone phosphinic acid, and alcohol converts it into an ethereal salt; it is soluble in ether and light petroleum. Nitric acid decomposes it, but not completely; when heated with bromine and water, the whole of the phosphorus is, however, converted into phosphoric acid. Zinc ethide has no action on it in the cold, but decomposes it at higher temperatures, forming a substance not yet investigated.

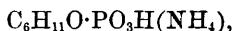
*Diacetone phosphorus chlorobromide*,  $C_6H_{10}O_2PClBr$ , is obtained by adding bromine to the chloride dissolved in light petroleum; it forms a colourless crystalline mass, fuming slightly in contact with air; it melts at  $142^\circ$ , is sparingly soluble in light petroleum, more easily in ether. Water decomposes this compound, converting it into mesitylene oxide, hydrochloric, hydrobromic, and phosphoric acids.

*Diacetone phosphorus trichloride*,  $C_6H_{10}O_2PCl_3$ , is formed when a current of dry chlorine is passed into a solution of the chloride in light petroleum; on evaporating, it separates as a colourless crystalline mass. It is less soluble in light petroleum and ether than the chlorobromide, and is more slowly attacked by water than this latter compound; it melts at  $115^\circ$ . Silver nitrate precipitates two-thirds of the chlorine from the aqueous solution of the trichloride; the remainder may, however, be removed by continued boiling. Its decomposition by water would therefore appear to take place in two stages.

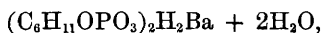
*Diacetonephosphinic acid* or *isopropylacetonylphosphinic acid*,  $CHMe_2 \cdot CH(COMe) \cdot PO(OH)_2 + H_2O$ , is obtained by decomposing diacetone phosphorus chloride with water and as a bye-product in the preparation of this chloride; it is soluble in water and alcohol, but only sparingly soluble in ether; it crystallises in fine needles containing 1 mol. of water, and melts at  $63^\circ$ . This acid resembles the chloride



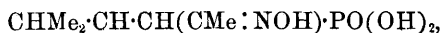
in its behaviour to nitric acid and to bromine and water; it is a dibasic acid. The following salts have been prepared:—The *potassium salt*,  $C_6H_{11}O \cdot PO_3HK$ , obtained by adding alcoholic potash to an alcoholic solution of the acid, forms a colourless resinous mass easily soluble in water and alcohol; if an excess of acid be used, the hydrogen salt,  $C_6H_{11}O \cdot PO_3HK + C_6H_{11}O \cdot PO_3H_2$ , separates out; it is soluble in water, but sparingly soluble in alcohol. The *ammonium salt*,



is soluble in water and almost insoluble in alcohol. When alcoholic ammonia is used a white crystalline precipitate is obtained of the salt  $(C_6H_{11}O \cdot PO_3)_2H(NH_4)_3 + 2H_2O$ . The *hydrogen barium salt*,



is obtained by boiling an aqueous solution of the acid with barium carbonate, and the normal salt by treating the acid with a solution of baryta; it crystallises in colourless leaflets containing 6 mols.  $H_2O$ . The calcium salts are prepared in the same manner as the barium salts; the normal salt is less soluble in hot water than in cold. The *magnesium salt*,  $C_6H_{11}O \cdot PO_3Mg + 6H_2O$ , forms lustrous plates. The *silver salt*,  $C_6H_{11}OPO_3Ag_2$ , is obtained as a white precipitate; it is soluble in ammonia and in nitric acid. The *lead salt*,  $C_6H_{11}OPO_3Pb$ , is a white precipitate. The existence of one carbonyl group in diacetonephosphinic acid is shown by its yielding one *oxime* only when treated with hydroxylamine. This compound,



forms colourless crystals, is soluble in water and in alcohol, but only sparingly in ether; it melts at  $169-170^\circ$  with decomposition, and is a strongly bibasic acid.

*Isopropylphosphino-carboxylic acid*,  $COOH \cdot CHMe \cdot CH_2 \cdot PO(OH)_2$ , is formed by oxidising diacetonephosphinic acid with fuming nitric acid; the product of this reaction is treated with baryta, and from the precipitate so obtained cold water extracts the barium salt of this acid. It is sparingly soluble in water and more soluble in cold than hot water; it crystallises in shining leaflets, and has the composition  $(C_4H_5PO_5)_2Ba_3$ . The *silver salt*,  $C_4H_5O_5Ag_3$ , is obtained as a white crystalline precipitate soluble in nitric acid and in ammonia. The free acid forms a colourless crystalline mass, soluble in water, alcohol, and ether. P. P. B.

**Compounds of Mercaptans with Aldehydes, Ketones, and Ketonic Acids.** By E. BAUMANN (*Ber.*, 18, 883—892).—In a former communication (this vol. p. 513), the author described the compounds formed by mercaptan and pyroracemic acid, one class of which may be regarded as simple additive products, whilst the other class are formed from the first by elimination of water. Compounds similar to the latter are obtained from aldehydes and ketones by passing hydrogen chloride into mixtures of mercaptans and aldehydes or ketones. These compounds obtained from aldehydes and mercaptans the author styles *mercaptals* or *thio-acetals*. The mercaptals are

stable compounds, but slightly attacked by acids or alkalis; are insoluble in water; the solid mercaptals may be purified by crystallisation from ether, light petroleum, or benzene, whilst those which are liquid at ordinary temperatures are obtained pure with difficulty, owing to their decomposition by heat.

*Ethylmercaptal of acetaldehyde*,  $\text{CHMe}(\text{SEt})_2$ , is a mobile highly refractive liquid, having an odour like that of thioaldehyde; *ethylmercaptal of benzaldehyde*,  $\text{CHPh}(\text{SEt})_2$ , and *phenylmercaptal of benzaldehyde*,  $\text{CHPh}(\text{SPh})_2$ , are both liquids. *Parabromophenylmercaptal of benzaldehyde*,  $\text{CHPh}(\text{SC}_6\text{H}_4\text{Br})_2$ , obtained from parabromophenyl mercaptan and benzaldehyde, crystallises from ether or alcohol in silky, lustrous needles, melting at  $79-80^\circ$ . *Phenylmercaptal of cinnamaldehyde*,  $\text{CHPh}:\text{CH}\cdot\text{CH}(\text{SPh})_2$ , crystallises in colourless shining needles, melting at  $80-81^\circ$ . *Parabromophenylmercaptal of cinnamaldehyde*,  $\text{CHPh}:\text{CH}\cdot\text{CH}(\text{SC}_6\text{H}_4\text{Br})_2$ , crystallises in long colourless needles, and melts at  $105-107^\circ$ .

*Phenylmercaptal of piperonal* crystallises from acetone in colourless crystals resembling benzoic acid, and melts at  $48^\circ$ .

Chloral does not form mercaptals, but unites directly with mercaptans, forming additive products. The additive compound of ethyl mercaptan and chloral has been described by Marius and Mendlessohn (*Ber.*, 3, 445). With phenyl mercaptan, chloral forms the compound  $\text{C}_2\text{HCl}_3\text{O} + \text{C}_6\text{H}_5\text{S}$ , which crystallises in transparent tablets melting at  $52-53^\circ$ , and is decomposed by aqueous alkalis in the cold into mercaptan, chloroform, and formic acid. The compound of parabromophenylmercaptan and chloral resembles the last-mentioned compound, and melts at  $72^\circ$ .

*Mercaptoles* is the name assigned by the author to the compounds formed from ketones and mercaptans. They are not as easily formed as the mercaptals, and in the preparation of mercaptols from aromatic ketones it is necessary to add zinc chloride to the mixture of ketone and mercaptan. The mercaptoles are stable compounds, resisting the action of acids and alkalis, are decomposed by heat, and are insoluble in water, but soluble in ether, alcohol, benzene, and glacial acetic acid.

*Ethylmercaptole of acetone*,  $\text{CMe}_2(\text{SEt})_2$ , is a light mobile liquid, decomposing when distilled. *Phenylmercaptole of acetone* is an oil, heavier than water. *Parabromophenylmercaptole of acetone*,



crystallises from ether in long transparent prisms, melting at  $89-90^\circ$ . *Phenylmercaptole of benzophenone*,  $\text{CPh}_2(\text{SPh})_2$ , crystallises from ether in short, lustrous prisms, melting at  $139^\circ$ , and when heated above its melting point becomes first green and finally brown.

Ethyl acetoacetate reacts with mercaptans, but less energetically than acetone; pyroracemic acid reacts not only with mercaptans but with thiactic acid, thioglycollic and xanthogenic acid, and other compounds containing the group  $\cdot\text{SH}'$ .

Isatin and benzoylformic acid unite with mercaptans, forming additive compounds.

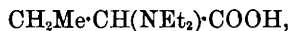
*Isatinphenylmercaptan*,  $\text{C}_8\text{H}_5\text{NO}_2 + \text{C}_6\text{H}_5\text{S}$ , is formed by adding

phenylmercaptan to an alcoholic solution of isatin, it is insoluble in water but soluble in alcohol and benzene, undergoing a partial decomposition into its constituents. It crystallises in yellowish silky needles.

*Phenylmercaptan-benzoylformic acid*,  $C_6H_5O_3 + C_6H_5S$ , obtained by adding phenylmercaptan to benzoyl formic acid, is purified by crystallisation from benzene; it melts at  $68.5^\circ$ . When treated with hydrogen chloride, it is resolved into *benzoylformic acid* and *phenylmercaptole of benzoylformic acid*,  $CPh(SPh)_2 \cdot COOH$ . This compound is sparingly soluble in benzene, crystallising from its solutions in transparent prisms melting at  $142^\circ$ .

Some of the above compounds on oxidation yield disulphones, the investigation of which is not yet completed. P. P. B.

**Diethyl-amido- $\alpha$ -butyric Acid.** By E. DUVILLIER (*Compt. rend.*, 100, 860—862).—Diethyl-amido- $\alpha$ -butyric acid,

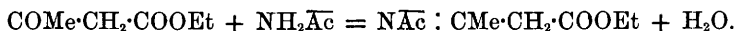


is obtained by the action of bromo- $\alpha$ -butyric acid (1 mol.) on a concentrated aqueous solution of diethylamine (3 mols). The crude product after separation from the diethylamine is digested for some days at about  $60^\circ$  with a large excess of cupric hydroxide suspended in water, and the solution concentrated on a water-bath. On cooling it deposits deep violet-red crystals of normal cupric diethylamido- $\alpha$ -butyrate, which can be purified by recrystallisation. To obtain the pure acid the copper salt is decomposed by hydrogen sulphide, the solution concentrated to a syrup, and finally placed over sulphuric acid. After some time, it solidifies to a crystalline highly deliquescent mass, which is extremely soluble in water, somewhat less soluble in absolute alcohol, only slightly soluble in ether. On adding ether to the alcoholic solution, the acid is precipitated in the form of an oil. When carefully heated, diethylamido- $\alpha$ -butyric acid melts at  $135^\circ$ , and sublimes slightly; at a higher temperature it distils, leaving a slight carbonaceous residue.

The normal cupric salt is the only salt of this acid which could be obtained pure and crystallised. It is very soluble in water and in alcohol, forming violet solutions resembling those of methyl-violet.

C. H. B.

**Ethyl Acetyl- $\beta$ -imidobutyrate.** By F. CANZONERI and G. SPICA (*Gazzetta*, 14, 491—492).—By heating acetamide and ethyl acetoacetate with a small quantity of aluminium chloride under reduced pressure there is produced *ethyl acetyl- $\beta$ -imidobutyrate*, derived from 1 mol. of each of the above substances with elimination of 1 mol.  $H_2O$ , thus:—



This compound melts at  $64$ — $65^\circ$ , and boils about  $225^\circ$ ; it crystallises in long needles, insoluble in cold, but readily soluble in hot water, alcohol, and ether. On boiling with concentrated acids or alkalis, it yields acetic acid and ethyl  $\beta$ -imidobutyrate, and finally ammonia.

V. H. V.

**Action of Alkylamines on Ethyl Acetoacetate.** By O. KUCKERT (*Ber.* **18**, 618—620).—When methylamine is passed into acetoacetic acid kept cooled at 0°, the additive product



is formed. This substance is a white solid, melting at 42—43°. At ordinary temperatures it undergoes decomposition, losing water and forming the compound  $\text{C}_7\text{H}_{13}\text{NO}_2$ . The latter is an oil which boils at 133° under 50 mm., or at 215° under normal pressure. Its formula must be either  $\text{NHMe} \cdot \text{CMe} : \text{CH} \cdot \text{COOEt}$ , or  $\text{NMe} : \text{CMe} \cdot \text{CH}_2 \cdot \text{COOEt}$ . This compound is formed at once if the acetoacetate is not kept well cooled. Diethylamine forms a similar compound, which must have the formula  $\text{NEt}_2 \cdot \text{CMe} : \text{CH} \cdot \text{COOEt}$ . This compound is an oil which boils at 160—163° under 20 mm. pressure.

When treated with paraldehyde and sulphuric acid, the methylamine-derivative forms a condensation product,  $\text{C}_{15}\text{H}_{23}\text{NO}_4$ . This gives fluorescent rhombic crystals melting at 86°. The diethylamine-derivative does not form a condensation product. L. T. T.

**Action of Amides on Ethyl Acetoacetate.** By F. CANZONERI and G. SPICA (*Gazzetta*, **14**, 448—453).—Formamide is heated with ethyl acetoacetate in presence of zinc chloride, the product dissolved in hydrochloric acid, then rendered alkaline with potash; the oil which separates, when subjected to fractional distillation, passes over for the greater part between 270—300°; it consists principally of ethyl lutidinemonocarboxylate,  $\text{C}_5\text{H}_2\text{NMe}_2 \cdot \text{COOEt}$ . It appears that ethyl lutidinedicarboxylate is first formed in accordance with the equation  $2\text{C}_6\text{H}_{10}\text{O}_3 + \text{CHONH}_2 - 3\text{H}_2\text{O} = \text{C}_{13}\text{H}_{17}\text{NO}_4$ , and from this the elements of carbonic anhydride and alcohol are eliminated with production of the ethylic salt of the monocarboxylic acid. In order to confirm this hypothesis, the substance was converted into the hydrochloride of the acid,  $\text{C}_5\text{H}_2\text{NMe}_2 \cdot \text{COOH} \cdot \text{HCl} + \text{H}_2\text{O}$ , which crystallises in transparent rhombohedra melting at 220° with evolution of pyridine vapours. The platinochloride,



was also prepared in the form of red crystals, very soluble in alcohol and water.

The portion of the product which boiled above 300° consisted of a substance of the empirical formula  $\text{C}_{12}\text{H}_{15}\text{NO}_2 = 2\text{C}_6\text{H}_{10}\text{O}_3 + \text{NH}_3 - 4\text{H}_2\text{O}$ , which crystallises in long silky needles melting at 78—80°; its hydrochloride and platinochloride are very soluble crystalline substances; the latter melts at 195—196°. Owing to the small quantity of material, its constitution could not be accurately ascertained.

V. H. V.

**Action of Ethyl Acetoacetate on the Amidines. Pyrimidines.** By A. PINNER (*Ber.*, **18**, 759—763).—The author substitutes the formula  $\text{R} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{C}(\text{OH}) \\ \text{N} : \text{CMe}_2 \end{smallmatrix} > \text{CH}$  for that previously assigned (this vol., p. 158), terming the nucleus,  $\text{C}_4\text{H}_4\text{N}_2$ , pyrimidine; he adds the following to the account of the derivatives of phenylmethylhydroxypyrimidine

there given. The platinochloride crystallises with 2 mols.  $\text{H}_2\text{O}$ . The dichromate,  $(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})_2\cdot\text{H}_2\text{Cr}_2\text{O}_7 + 5\text{H}_2\text{O}$ , forms thick, orange-red prisms, and melts at  $177^\circ$ . The picrate,  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$ , crystallises in silky, yellow needles and melts at  $189^\circ$ . The acetyl-derivative,  $\text{C}_{11}\text{H}_9\text{AcN}_2\text{O}$ , is obtained as a crystalline mass melting at  $40\text{--}41^\circ$ .

A. J. G.

**Additive Product of Methylamine and  $\beta$ -Methylglycidic Acid.** By N. FIELINSKY (*J. Russ. Chem. Soc.*, 1884 (1), 687—688).

—On heating  $\beta$ -methylglycidic acid,  $\begin{array}{c} \text{CH}_3\cdot\text{CH} \\ | \\ \text{COOH}\cdot\text{CH} \end{array} \text{O}$ , prepared by Melikoff's method (*Abstr.*, 1883, 969), with methylamine, a crystalline acid of the composition  $\text{C}_5\text{H}_{11}\text{NO}$ , is obtained. The analogous reaction of ammonia with  $\beta$ -methylglycidic acid makes it probable that the compound formed in this instance is methylamidohydroxybutyric acid.

A. T.

**Oxidation of Acids of the Lactic Series.** By V. ARISTOFF (*J. Russ. Chem. Soc.*, 1884 [2], 249).—Pyroracemic acid was found amongst the products of the oxidation of hydroxypropionic acid with potassium permanganate in sulphuric acid solution, whence it is deduced that ketonic acids are the primary oxidation products of the  $\alpha$ -hydroxy-acids.

A. T.

**Preparation of Thiolactic Acid.** By C. BÖTTINGER (*Ber.*, 18, 486).—Pyruvic acid is heated with an excess of ammonium sulphide for two hours at  $110^\circ$ , the product diluted with water, acidulated with sulphuric acid, and extracted with ether; the thiolactic acid obtained is purified by conversion into its ethyl or metallic salts. It is free from thiodilactylic and dithiodilactylic acids.

A. K. M.

**Decomposition of Ferrous Oxalate.** By S. BIRNIE (*Chem. Centr.*, 1884, 85).—When crystallised ferrous oxalate is heated to rather above  $100^\circ$ , in a current of nitrogen, it loses some water of crystallisation, and suffers slight decomposition. Below  $200^\circ$  all the water of crystallisation is expelled. Above  $330^\circ$  the salt is entirely decomposed; steam, carbonic oxide and anhydride, escape, and the residue consists principally of ferrous oxide with a small quantity of carbon and metallic iron, the latter originating from the action of the carbon on the ferrous oxide. The ferrous oxide after being heated at  $300\text{--}400^\circ$ , loses the property of spontaneously inflaming in the air. Ferrous oxalate heated in a current of hydrogen, at first is decomposed as in a stream of nitrogen. At  $340^\circ$  the salt is entirely decomposed, with formation of carbonic oxide, anhydride, and ferrous oxide; near  $370^\circ$  the latter is reduced by the hydrogen to the metallic state. The residue also contains from 1—2 per cent. of free carbon. The metallic iron produced at  $435^\circ$  still inflames in air, but ceases to do so after heating at  $470^\circ$ . The pyrophoric iron perceptibly decomposes water below  $10^\circ$ , and rapidly between  $50\text{--}60^\circ$ . The pyrophoric property is

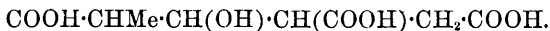
apparently unconnected with occluded gases and the presence of free carbon, and is solely dependent on a state of fine division.

W. R. D.

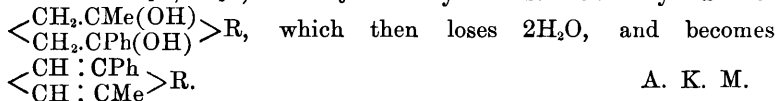
**Formation of Pyrotartaric Acid.** By E. ERLÉNMEYER (*Ber.*, **18**, 994—996).—In reply to Böttinger (this vol., p. 78), the author states that his view of the formation of pyrotartaric acid from pyruvic acid is the following: 2 molecules of pyruvic acid first unite to form  $\text{COOH}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{COOH}$ , which parts with the elements of water, and becomes  $\text{COOH}\cdot\text{CMe}:\text{CH}\cdot\text{CO}\cdot\text{COOH}$ ; this then reunites with the elements of water with formation of



which changes to the unstable  $\beta$ -lactone, and then (with separation of carbonic anhydride) to the compound  $\text{COOH}\cdot\text{CHMe}\cdot\text{CH}:\text{CO}$ . By the addition of the elements of water to the last compound, the formula,  $\text{COOH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{COOH}$ , of pyrotartaric acid is arrived at. Its formation from glyceric acid may be explained by the assumption of the previous formation of pyruvic acid. Böttinger's syrupy acid may be assumed to be derived from a tripyruvic acid, just as pyrotartaric acid is derived from a dipyruvic acid, and to have one of the two formulæ,  $\text{COOH}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}(\text{COOH})\cdot\text{CH}_2\cdot\text{COOH}$ , or



With regard to the formation of furfurane, thiophen, and pyrroline-derivatives from acetophenoneacetone (this vol., p. 516), the action of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_3\text{NH}$  may be assumed to yield first



A. K. M.

**Pyrocinchonic and Dichloradipic Acids obtained from  $\alpha$ -Dichloropropionic Acid.** By R. OTTO and H. BECKURTS (*Ber.*, **18**, 825—847, and 847—859).—In former communications, the authors have shown that, by the action of molecular silver upon  $\alpha$ -dichloropropionic acid dissolved in benzene, a dichloradipic acid, and an acid isomeric with hydromuconic acid, are formed. This latter acid is identical with Weidel and Schmidt's pyrocinchonic acid (*Abstr.*, 1879, 947; *Annalen*, **173**, 76), Weidel and Brix's (*Abstr.*, 1882, 1304), and that found by Roser amongst the products of oxidation of oil of turpentine (*Ber.*, **14**, 1318; *Abstr.*, 1882, 1114), also with Schwanert's meta- and pyro-camphoresinic acids (*Annalen*, **128**, 77).

*Pyrocinchonic acid* cannot be isolated, since whenever it is formed it immediately decomposes into the anhydride. The authors give a description of this anhydride and the salts of the acid, which in the main confirm the accounts of Roser and of Weidel and Brix (*loc. cit.*). Pyrocinchonic anhydride is oxidised by potassium dichromate and sulphuric acid, yielding carbon dioxide and acetic acid. Pyrocinchonic acid can be obtained from  $\alpha$ -dibromopropionic acid in the same manner as it is obtained from the chloro-acid. The production of pyrocinchonic acid from  $\alpha$ -dichloro- and  $\alpha$ -dibromopropionic acids makes it

probable that this acid is  $\alpha$ -dimethylacetylenedicarboxylic acid, and its behaviour on oxidation, together with its easy conversion into the anhydride, make it probable that it is *dimethylmaleic acid*, and isomeric with the homitaconic acid described by Markownikoff and Krestownikoff (Abstr., 1880, 238, and 1881, 1127). The attempts made to convert pyrocinchonic acid into its isomeride have been without success.

Pyrocinchonic anhydride when heated with hydriodic acid in sealed tubes at  $220^{\circ}$ , is converted into two *butylenedicarboxylic* or *adipic acids*. One of these, the less soluble of the two, melts at  $193$ — $194^{\circ}$ , and is thereby converted into its anhydride (m. p.  $186$ — $187^{\circ}$ ); it is identical with the compound obtained in a similar manner by Roser (Ber., 16, 2012), also with Weidel and Brix's *hydropyrocinchonic acid* (loc. cit.), and von Meyer's *isoadipic acid* (J. pr. Chem. [2], 26, 337). The second adipic acid forms colourless, transparent, prismatic crystals; it is easily soluble in water, alcohol, and ether, and melts at  $118$ — $120^{\circ}$ . Its silver salt,  $C_6H_8O_4Ag_2$ , is obtained as a white crystalline precipitate, on adding silver nitrate to an aqueous solution of its ammonium salt, which solution gives no precipitates with barium chloride, magnesium sulphate, nickel sulphate, cobalt nitrate, or manganese sulphate, but immediate precipitates are obtained with lead acetate, ferric chloride, and mercuric chloride, and precipitates after some time with zinc sulphate, copper sulphate, and calcium chloride. The acid is apparently the *ethylmethylmalonic acid*,  $CEtMe(COOH)_2$ , described by Conrad and Bischoff (Annalen, 204, 145). When pyrocinchonic acid is reduced by sodium amalgam, besides the above *butylenedicarboxylic acids*, a third is formed, melting at  $240$ — $241^{\circ}$ . This same acid is obtained when the anhydride of the adipic acid melting at  $193$ — $194^{\circ}$  is dissolved in hot water. Pyrocinchonic acid dissolves zinc without evolution of hydrogen, and yields a solution of zinc pyrocinchonate and the zinc salt of the adipic acid melting at  $193$ — $194^{\circ}$ . In this respect it resembles maleic acid, which dissolves zinc, forming solutions of zinc maleate and succinate. The authors consider this fact to indicate that the adipic acid, melting at  $193$ — $194^{\circ}$ , is the symmetrical *dimethylsuccinic acid*, a conclusion supported by the production of this same acid by the action of molecular silver on  $\alpha$ -bromopropionic acid. The relation of this acid to its isomeride, melting at  $240$ — $241^{\circ}$ , is probably similar to that existing between maleic and fumaric acids, a view which is supported by the formation of the second acid by the action of water on the anhydride of the first. The dibenzyl-dicarboxylic acids obtained by Reimer from stilbenedicarboxylic acid (Abstr., 1882, 200), may also be transformed in a similar manner.

*Dichloradipic acid*,  $C_6H_8Cl_2O_4$ , the formation of which from  $\alpha$ -dichloropropionic acid is described above, crystallises from benzene in small ill-defined crystals, from water in crusts; it is almost insoluble in cold benzene, more easily soluble in hot benzene, is soluble in water, in alcohol, and in ether; it melts at  $185^{\circ}$ . The salts of this acid are very unstable. The *sodium* salt crystallises in lustrous leaflets having the composition  $C_6H_6Cl_2O_4Na_2$ ; the *potassium* salt crystallises with 2 mols.  $H_2O$ , and has the formula  $C_6H_6Cl_2O_4K_2 + 2H_2O$ ;

both are sparingly soluble in alcohol. The *silver salt*,  $C_6H_4Cl_2O_4Ag_2$ , is obtained as a white crystalline precipitate. This compound when heated with water is decomposed into silver chloride, carbonic anhydride, and the silver salt of an acid which appears to be a *chlorotiglic acid*. Chloradipic acid undergoes a similar decomposition when heated with alcoholic potash. This new acid,  $C_6H_7ClO_4$ , crystallises in white, shining leaflets, which are easily soluble in alcohol, ether, and chloroform, less soluble in hot water, and almost insoluble in cold water. It melts at  $68-69^\circ$ , can be sublimed without decomposing, and is volatile in steam.

Dichloradipic acid can be converted into pyrocinchonic anhydride by heating its solution in benzene with molecular silver.

When an aqueous solution of dichloradipic acid is reduced by sodium amalgam, the two adipic acids melting respectively at  $193-194^\circ$  and at  $240-241^\circ$  are produced. By the action of zinc and sulphuric acid on alcoholic solutions of dichloradipic acids, the adipic acid melting at  $193-194^\circ$  is formed together with another adipic acid, which crystallises in small white leaflets melting at  $97-98^\circ$ . This acid the authors consider to be identical with *propylmalonic acid* described by Tate (*Inaug. Diss.*, Würzburg, 1879). Together with these acids a third appears to be formed, possibly the adipic acid which melts at  $118-120^\circ$ . Attempts made to convert dichloradipic acid into  $\alpha$ -dichloropropionic acid, by acting on it with chlorine, have been without success.

P. P. B.

**Derivatives of Normal Suberic Acid.** By C. HELL and R. REMPEL (*Ber.*, 18, 812-823).—The brominated product obtained by heating suberic acid with  $\frac{1}{1000}$  of its weight of amorphous phosphorus and half its weight of bromine in a sealed tube, consists of a mixture of unaltered suberic acid, with the mono- and di-bromo-derivatives. The separation and purification of the bromine-derivatives is very troublesome.

*Monobromosuberic acid* is a white crystalline substance; it melts at  $100-101^\circ$ , is decomposed at  $140-150^\circ$ , giving off hydrobromic acid; it is extremely soluble in ether, alcohol, benzene, light petroleum, and carbon bisulphide, moderately in chloroform, and almost insoluble in cold water. On stirring up with water at a temperature of about  $30-35^\circ$ , however, it forms an oily liquid. By acting on monobromosuberic acid with alcoholic potash, a mixture of ethoxy- and hydroxy-suberic acids is obtained, with traces of a compound,  $C_8H_{10}O_4$ , to which the authors have given the name of subercolic acid.

*Ethoxysuberic acid*,  $EtO \cdot C_6H_{11}(COOH)_2$ , is a light yellow syrup readily soluble in alcohol, ether, and water, it does not crystallise even on cooling to below  $-40^\circ$ ; on distillation it begins to decompose at  $130^\circ$ , carbonic anhydride and water being given off, and yields a mobile oil, having a penetrating but pleasant odour; it boils at  $230-300^\circ$ . The *silver salt*,  $C_{10}H_{16}O_5Ag_2$ , is obtained as a voluminous slimy precipitate, which forms a brittle yellowish horn-like mass when dry. The *barium salt*,  $C_{10}H_{16}O_5Ba$ , is obtained as a gummy mass which by long drying over sulphuric acid forms a white crystalline powder. The *lead salt* forms a curdy white precipitate which softens



on heating, but becomes crystalline in the cold; it is somewhat soluble in water, but insoluble in ether. The *zinc salt*,  $C_{10}H_{16}O_5Zn$ , is readily soluble in cold water, from which solution it is partially precipitated on warming. The copper salt was prepared.

*Hydroxysuberic acid*,  $HO \cdot C_8H_{11}(COOH)_2$ , is obtained with the ethoxy-compound, and is separated from it by converting them both into the zinc salts, and dissolving out the ethoxy-salt with water, the hydroxy-salt being almost insoluble. Hydroxysuberic acid may also be obtained pure by the action of aqueous alkalis on monobromosuberic acid; it forms dazzlingly white crystalline concretions, has a strongly acid taste, melts at  $110-112^\circ$ ; by continued heating between  $110^\circ$  and  $120^\circ$ , it loses 1 mol.  $H_2O$ , and forms a gummy viscous anhydride, which has a faintly acid and astringent taste. By dry distillation the acid is decomposed at  $190-200^\circ$ , carbonic anhydride and water being given off, and an oily body of peculiar odour formed. Hydroxysuberic acid is not very soluble in cold water, but readily in hot. The *zinc salt*,  $C_8H_{12}O_5Zn + 2\frac{1}{2}H_2O$ , is obtained as a white crystalline precipitate. The *magnesium salt*,  $C_8H_{12}O_5Mg + H_2O$ , forms a voluminous white crystalline powder. The *silver salt*,  $C_8H_{12}O_5Ag_2$ , is a stable white crystalline compound. The *copper salt*,  $C_8H_{12}O_5Cu$ , is obtained in dark green scales. The nickel, barium, and calcium salts were also prepared. *Subercolic acid* forms a fine white powder; it sublimes at  $225-230^\circ$  without melting, but is partially decomposed, forming long hair-like needles; it combines with bromine, forming an oil which has an agreeable odour, and is soluble in water and ether. The *silver salt*,  $C_8H_8O_4Ag_2$ , is obtained as a fine white powder, it is not acted upon by light. The *barium salt*,  $C_8H_8O_4Ba$ , is obtained in fine tabular crystals. The *calcium salt*,  $C_8H_8O_4Ca$ , is similar, but is less soluble in water. The *magnesium salt* forms brilliant scales; it is very soluble in water. This acid appears to be somewhat analogous to the dicarboxylic acids of the aromatic series, as it sublimes without fusion.

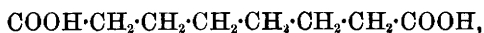
By acting on dibromosuberic acid with alcoholic potash, a mixture of diethoxysuberic and dihydroxysuberic acids is obtained. The *diethoxy-acid*,  $C_8H_{10}(OEt)_2(COOH)_2$ , is isolated by repeatedly shaking the aqueous solution of the mixed acids with a small quantity of ether; it is very similar to the monethoxy-acid, and like it forms a yellow uncrystallisable syrup. which is, however, slightly more viscous; it is readily soluble in water, ether, and alcohol, but is insoluble in concentrated salt solutions. The *silver salt*,  $C_{12}H_{20}O_8Ag_2$ , is obtained as a voluminous white very finely divided precipitate. The *zinc salt* is readily soluble in water, but is less soluble in hot than in cold.

Although nitric acid has hardly any action on suberic acid, it acts readily on the hydroxy- and ethoxy-compounds, adipic and oxalic acids being formed.

A. P.

**Derivatives of Suberic Acid.** By HEMPEL (*Chem. Centr.*, 1884, 215—216).—The monobromosuberic acid of Ganttner and Hell is not a pure substance, but is contaminated with dibromosuberic acid and unchanged suberic acid. It was further purified by chloroform. By the action of alcoholic potash on monobromosuberic acid *ethoxysuberic*

and *hydroxysuberic* acids were obtained. Ethoxysuberic acid is syrupy and uncrystallisable, and its salts crystallise with difficulty. Hydroxysuberic acid, which is also formed by the action of aqueous potash, crystallises well, and forms characteristic salts. By heating at  $110^{\circ}$  it yields an anhydride. Dibromosuberic acid when acted on by alcoholic potash, yields diethoxysuberic acid, dihydroxysuberic acid, and an acid of the formula  $C_8H_{10}O_4$ . Diethoxysuberic acid resembles ethoxysuberic acid, and crystallises badly. The acid of the formula  $C_8H_{10}O_4$  is sparingly soluble in water, and sublimes at  $230^{\circ}$ , apparently without previous fusion. It forms well-crystallised salts, and is probably a *tetrahydrophthalic acid*. When hydroxysuberic acid is oxidised with nitric acid, adipic acid is formed. Suberic acid has therefore the normal structure



and hydroxysuberic acid is a  $\beta$ -hydroxy-acid,



W. R. D.

### Normal Pentylmalonic Acid, an Isomeric Suberic Acid.

By C. HELL and G. SCHÜLE (*Ber.*, **18**, 624—628).—Four suberic acids have been hitherto obtained, of which the constitution of two is known, of two unknown. The author has now prepared a fifth by means of cyanænanthyllic acid.

Enanthylic acid was converted into the monobromo-derivative, which was purified by conversion into the ethereal salt and fractionation in a current of steam.

*Ethyl  $\alpha$ -monobromænanthylate* is a colourless, highly refractive liquid of fruity odour. It boils, with partial decomposition, at  $220$ — $225^{\circ}$ , and may be distilled in a current of steam. This salt is then digested with an alcoholic solution of potassium cyanide, and the product boiled with potash. *Pentylmalonic acid* thus obtained crystallises in colourless, triclinic prisms, which melt at  $82^{\circ}$ , and decompose at  $129$ — $140^{\circ}$  into enanthylic acid and carbonic anhydride. This decomposition shows that the acid is pentylmalonic acid, and that the monobromænanthyllic acid is the  $\alpha$ -compound, and not a  $\zeta$ -derivative, as believed by Helms (*Ber.*, **18**, 1167). Pentylmalonic acid is easily soluble in water, alcohol, and ether. Its *silver, barium, strontium, calcium, and cadmium salts* are described.

L. T. T.

**Rate of Formation of Maleïc Anhydride.** By L. T. REICHER (*Chem. Centr.*, 1884, 87—90).—Schwab has shown that when fumaric and maleïc acids are heated with a large excess of ethyl alcohol for eight hours at  $100^{\circ}$ , the former is etherified to the extent of 3 per cent., but the latter to the extent of 44.9 per cent. This abnormal behaviour of maleïc acid he attributed to its partial conversion into maleïc anhydride, so that the etherification is the result of the two changes (1)  $C_4H_4O_4 + 2C_2H_5O = C_6H_{12}O_4 + 2H_2O$ ; (2)  $C_4H_4O_4 = C_4H_2O_3 + H_2O$  and  $C_4H_2O_3 + 2C_2H_5O = C_6H_{12}O_4 + H_2O$ . On the other hand Menshutkin regards the result as due to the difference in the constitution of the two acids. In order to decide the question, the

author has studied the behaviour of maleic acid at  $100^{\circ}$ , and finds that when it is heated at this temperature in a vacuum, it is converted with loss of water into maleic anhydride. A determination of the vapour-density at this temperature corresponded with that of a mixture of maleic anhydride and water. A series of determinations show that after heating the acid at  $100^{\circ}$  for one hour, 11.6 per cent., and for eleven and a half hours 91.3 per cent., of maleic anhydride is formed. The author's results are thus corroborative of Schwab's conclusion.

W. R. D.

**Condensation-products of Pyruvic Acid.** By C. BÖTTINGER (*Ber.*, **18**, 609—611).—In their researches on halogen derivatives of acrylic acid, R. Otto and H. Beckurt (*Ber.*, **18**, 241) noticed that when potash acts on  $\alpha$ -dichloropropionic acid, considerable quantities of a non-crystallisable acid were often obtained, which they considered as identical with, or closely allied to, "Tollens' acryl-colloids," and as probably a condensation-product of pyruvic acid.

The author also obtained a syrupy acid as a bye-product when preparing pyrotartaric from pyruvic acid. This acid does not distil without decomposition, nor is it volatile in steam. Its salts are indefinite, and do not crystallise. Salts were obtained approximating to the formulæ  $C_5H_5Pb_3O_7$ ,  $C_5H_5Ba_3O_7$ ,  $C_5H_5Zn_3O_7$ , and  $C_5H_5Zn_2O_7$ . From the last salt, the author is inclined to regard the acid as in some way formed by a union of pyrotartaric and pyruvic acids.

L. T. T.

**Condensation-products of  $\alpha$ -Ketonic Acids.** By B. HOMOLKA (*Ber.*, **18**, 987—989).—On mixing pyruvic acid (1 part) with acetic anhydride (4—5 parts), and dehydrated sodium acetate (5 parts), carbonic anhydride is evolved, and the temperature gradually rises; the mixture should, however, be heated rapidly, in order to complete the reaction. The product is extracted with boiling light petroleum (b. p.  $50$ — $60^{\circ}$ ), which after filtration and evaporation deposits colourless prisms of  $\alpha$ -crotonic acid, melting at  $70$ — $71^{\circ}$ . Phenylglyoxylic acid yields a perfectly analogous reaction, the product being a very sparingly soluble acid, melting at  $130$ — $132^{\circ}$ , evidently cinnamic acid.

Phenylglyoxylic acid yields a condensation-product with dimethylaniline and zinc chloride, which, as Peter has also shown, is tetramethyldiamidotriphenylmethane, the leuco-base of malachite-green. Pyruvic acid also yields a basic condensation-product with dimethylaniline and zinc chloride; in acid solution it is converted by chloranil, manganese dioxide, and other oxidising agents, into a dirty green dye. When phenylglyoxylic acid is heated with phenol and sulphuric acid at  $120^{\circ}$ , carbonic anhydride is evolved; on treating the product with water a red crystalline substance is obtained having the properties of benzaurin. Pyruvic acid behaves in the same way.

Isatin also yields crystalline condensation-products with dimethylaniline and with phenols, those from dimethylaniline being converted into bluish-green dyes by acid oxidising agents, and those from phenols into magnificent red dyes by alkaline ferricyanide.

A. K. M.

**Preparation of Tartronic Acid.** By A. PINNER (*Ber.*, **18**, 752—756).—Tartronic acid is most conveniently prepared by slowly adding ethyl trichlorolactate (1 mol.) to 10 per cent. aqueous soda (somewhat less than 5 mols.), heated at about 60—70°. After remaining for a short time, dilute acetic acid is added to faintly acid reaction, and the tartronic acid precipitated by barium chloride. The yield of barium tartronate is about 50 per cent. of the ethyl salt employed. A still better yield is obtained by employing baryta-water instead of aqueous soda.

Only the alkali salts of tartronic acid appear to be readily soluble in water. The barium salt,  $C_3H_2O_5Ba + 2H_2O$ , and the calcium salt,  $C_3H_2O_5Ca + 2\frac{1}{2}H_2O$ , are both microcrystalline. *Ethyl tartronate*,  $C_3H_2O_5Et_2$ , is an oil boiling at about 220°. A. J. G.

**Occurrence of Glutamine in the Sugar-beet and its Optical Behaviour.** By E. SCHULZE and E. BOSSHARD (*Ber.*, **18**, 390—391). The separation of glutamine from the sap of the beetroot has been described by the authors (*Abstr.*, 1883, 658). They have now succeeded in obtaining it from the variety known as the sugar-beet.

An aqueous solution of glutamine (4 grams in 100 c.c.) exhibits no appreciable rotatory power, whilst a solution containing 1 gram glutamine and 0.09 gram sulphuric acid in 20 c.c. in a 200 mm. tube rotates + 3°. A solution containing 0.541 gram glutamine and 0.06 gram oxalic acid in 20 c.c. exhibits a rotatory power of + 1°. In estimating the sugar in beet-juice, the error due to the presence of glutamine will, however, be small, and will only amount to a few tenths of a degree. A. K. M.

**Optical Behaviour of some Amido-acids.** By E. SCHULZE and F. BOSSHARD (*Ber.*, **18**, 388—389).—The authors refer to their experiments showing the formation of an optically active amido-acid by the action of hydrochloric acid and of an inactive amido-acid by the action of baryta-water on conglutin (*Abstr.*, 1884, 1306); also to Lewkowitsch's experiments on the separation of inactive mandelic acid into the dextro- and lævo-rotatory modifications by the action of *Pencillium glaucum*. By the action of this organism on inactive leucine and inactive glutaminic acid, the authors likewise obtain products which when dissolved in hydrochloric acid are *levorotatory*, the ordinary isomerides being *dextrorotatory*. When leucine is heated with baryta-water at 150—160° under pressure, it becomes inactive; aspartic acid was shown by Michael and Wing to undergo a similar change when heated with hydrochloric acid (*this vol.*, p. 377), so that it may be assumed that the formation of inactive products by the action of baryta-water on conglutin was due to the high temperature, 150—160°. A. K. M.

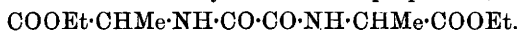
**Polyacetylene Compounds.** By A. BAEYER (*Ber.*, **18**, 674—681).—*Diacetylenedicarboxylic acid*,  $COOH \cdot C \equiv C \cdot C \equiv C \cdot COOH$ , is obtained by oxidation of the copper compound of ethyl propargylate with an alkaline solution of potassium ferricyanide. It crystallises with 1 mol.  $H_2O$  in rhombic tables or needles; it turns brown at 100°, and explodes

violently at about  $177^{\circ}$ ; this seems to be the first instance of an explosive substance containing carbon, hydrogen, and oxygen only. On exposure to light, the acid at first assumes a deep rose colour; on longer exposure it is converted into a purple-red mass. It is readily soluble in ether, alcohol, and chloroform, moderately in water, very sparingly in light petroleum and benzene. With an ammoniacal copper solution, the aqueous solution gives a brownish-red precipitate; with silver nitrate, a white turbidity; and with lead acetate and mercuric nitrate white precipitates. When treated with sodium amalgam, the acid yields first hydromuconic acid, and finally adipic acid.

When the aqueous solution of an acid salt of diacetylenedicarboxylic acid is heated, carbonic anhydride is evolved; after acidifying, the liquid yields to ether a crystalline acid; this with ammoniacal cuprous chloride gives a yellow precipitate, which soon turns red, and resembles cuprous acetylde.

A. J. G.

**Oxaldiamidopropionic Acid.** By H. SCHIFF (*Ber.*, 18, 490—491).—The formation of a crystalline compound, melting at  $135$ — $138^{\circ}$ , by the action of ethyl oxalate on alanine, has been previously mentioned (*Abstr.*, 1884, 907 and 995). If 5—10 per cent. of alcohol be added to the ethyl oxalate, the action of the alanine takes place more slowly, but the evolution of carbonic anhydride is reduced, and the resulting compound loses the property of readily eliminating ethylamine. The product is found to consist of two very similar isomeric substances, separable by fractional crystallisation, first from ether, and then from alcohol. The more sparingly soluble portion (10—12 per cent.) forms long lustrous needles, melting at  $152$ — $154^{\circ}$ , whilst the more abundant constituent forms more scaly crystals, melting at  $125$ — $127^{\circ}$ . The behaviour and composition of these compounds correspond with those of diethyl oxaldiamidopropionate,



When boiled with dilute hydrochloric acid, alcohol, oxalic acid, and alanine hydrochloride are produced.

The chief product of the action of ethyl oxalate on alanine is the non-crystalline acid previously mentioned (*loc. cit.*); this is found to contain several substances; monethyl oxaldiamidopropionate, the ethylamide of this, and the two oxaldiamidopropionic acids, appear to be present.

Aniline does not react with alanine, even on boiling, but with the above ethereal salts it yields oxaldianilide and aniline derivatives of alanine.

A. K. M.

**Synthesis of Allantoxanic Acid from Parabanic Acid.** By J. PONOMAREFF (*Ber.*, 18, 981—983).—The author gave reasons for believing that allantoxanic acid and allantoxaidine are closely related to parabanic acid (*Abstr.*, 1879, 226), and he now confirms this by the conversion of the latter compound into allantoxanic acid. On heating carbamide with parabanic acid, Grimaux (*Abstr.*, 1880, 105) obtained a compound,  $\text{C}_4\text{H}_6\text{N}_4\text{O}_4$ , of the same composition as ammonium allantoxanate, but of different properties; its alkaline solution gave the biuret reaction with copper solution. The author treats this com-

pound with potash solution of 1.3 sp. gr. which dissolves it with liberation of ammonia; on acidifying the alkaline solution with acetic acid, a crystalline precipitate is produced, and on crystallising this from boiling water, the characteristic silky needles of potassium allantoxanate,  $C_4H_2N_3O_4K$ , are obtained. In order to confirm this, other salts were prepared. On boiling the potassium salt with water, carbonic anhydride, biuret, and formic acid are produced. The relation of allantoxanic to parabanic acid and to oxalic acid is further confirmed by the production of oxalic acid on boiling allantoxanic acid with an excess of potash solution. A. K. M.

**Dehydracetic Acid.** By L. HAITINGER (*Ber.*, **18**, 452—453).—When dehydracetic acid is treated with aqueous ammonia at  $100^\circ$ , two substances are formed of the formulæ  $C_8H_9NO_3$  and  $C_7H_9NO$ . The compound  $C_8H_9NO_3$  is an acid which breaks up when heated into carbonic anhydride and the second substance  $C_7H_9NO$ ; this is a weak base, yields a readily soluble platinochloride and a dibromo-substitution product. In its chemical and physical properties it resembles the hydroxypyridine obtained from ammonchelidonic acid; in its composition it corresponds with hydroxylutidine, and when distilled with zinc-dust it yields a lutidine,  $C_7H_9N$ , boiling at  $147$ — $151^\circ$ . The analogy indicated by these results between chelidonic and dehydracetic acids is more apparent in the products of their decomposition on boiling with alkalis; dehydracetic acid (this *Journ.*, 1876, ii, 69) yielding 2 mols. acetic acid, 1 mol. acetone, and 1 mol. carbonic anhydride, whilst chelidonic acid (*Abstr.*, 1883, 870) yields 2 mols. oxalic acid and 1 mol. acetone. If the two carboxyl-groups in chelidonic acid (*loc. cit.*) be assumed to be replaced by methyl-groups and likewise a hydrogen-atom by carboxyl, the formula  $CMe \begin{smallmatrix} O \cdot CMe \\ \diagdown \quad \diagup \\ CH-CO \end{smallmatrix} C \cdot COOH$  is arrived at for dehydracetic acid, which is identical with that proposed by Perkin (this vol., p. 315). The author thinks it possible that the hydroxylamine and phenylhydrazine compounds have not the constitution ascribed to them by Perkin, but may be in some way connected with pyridine derivatives (*Abstr.*, 1884, 1302, 1196). A. K. M.

**Action of Aniline on Methyl Dehydracetate.** By W. H. PERKIN, JUN. (*Ber.*, **18**, 682—684).—When aniline is added to a solution of methyl dehydracetate in methyl alcohol, and the mixture gently warmed for about  $\frac{1}{4}$  minute, the product treated with water, and the whole allowed to remain for 12 hours, a small quantity of long colourless needles of a compound,  $C_{18}H_{15}NO_3 = CMe \begin{smallmatrix} CH-CO \\ \diagdown \quad \diagup \\ NPh \cdot CMe \end{smallmatrix} C \cdot COOMe$ , separates; it melts at  $152^\circ$ , is insoluble in water and sodium carbonate, but readily soluble in benzene and alcohol.

The main product of the reaction still remains in the mother-liquor, from which it cannot be recovered by evaporation, as it is completely converted into an intense orange-yellow dye, probably a condensation product. The mother-liquor is therefore acidulated with hydrochloric acid, and evaporated on the water-bath to a syrup; this is treated with an excess of aqueous potash, and allowed to remain for six hours,

when a considerable quantity of a crystalline substance separates, and is purified by recrystallisation. This substance has the formula  $C_{13}H_{13}NO$ ; it is undoubtedly formed from the compound  $C_{16}H_{15}NO_3$  by saponification and elimination of carbonic anhydride, and has therefore the constitution  $CO < \begin{smallmatrix} CH:CM_e \\ CH:CM_e \end{smallmatrix} > NPh$ . It crystallises in colourless needles, melts at  $197^\circ$ , and is readily soluble in hot water and alcohol, sparingly soluble in benzene. It can be distilled. The *platinochloride*,  $(C_{13}H_{13}NO)_2PtCl_6$ , crystallises in yellow needles.

A. J. G.

**Remarks on Perkin's Note on the Action of Aniline on Methyl Dehydracetate.** By L. HAITINGER (*Ber.*, 18, 1018—1019).

**Furfurane-derivatives.** By H. B. HILL and G. T. HARTSHORN (*Ber.*, 18, 448—451). When bromine (1 mol.) is added to a solution of monobromopyromucic acid in an excess of alkali, dibromofurfurane,  $C_4H_2Br_2O$ , is thrown down as a heavy colourless oil of aromatic odour. It is washed out of contact with air, dried, and distilled under diminished pressure, and in a current of carbonic anhydride. *α-Dibromofurfurane* boils at  $62-63^\circ$  under a pressure of 15 mm., and at  $164-165^\circ$  under atmospheric pressure (764 mm.) in a current of hydrogen. It solidifies at  $7-8^\circ$ , and melts at  $9-10^\circ$ ; it becomes oxidised by exposure to the air, with formation of an amorphous indifferent insoluble substance, the formula of which appears to be  $C_4H_2Br_2O_2$ . When the oil is covered with a layer of water, and exposed to the action of the air, a strongly acid liquid is obtained, containing hydrochloric, maleic, and apparently also fumaric acid.

Dilute nitric acid acts violently on dibromofurfurane, with production of fumaric acid, whilst maleic acid appears to be also formed when the reaction takes place in the cold. *α-Dibromofurfurane* combines readily with bromine to form the tetrabromide (m. p.  $110-111^\circ$ ) described by Hill (*Abstr.*, 1883, 912). This is however more readily obtained by adding an excess of bromine to an alkaline solution of monobromopyromucic acid; a compound melting at about  $55^\circ$  is also produced, and appears to be an isomeric *dibromofurfurane tetrabromide*,  $C_4H_2Br_6O$ . When the tetrabromide melting at  $110-111^\circ$  is boiled with water, it gradually dissolves, and the solution is found to contain monobromofumaric acid,  $C_4H_3BrO_4$ , and monobromomaleic acid, but if calcium carbonate is added so as to neutralise the hydrobromic acid as it is formed, monobromomaleic acid alone is obtained. This formation of the latter acid from the *α*-tetrabromide points to a near relationship between the tetrabromide and ordinary dibromosuccinic acid, but it is converted by fuming nitric in the cold into isodibromosuccinic acid. The isomeric *β*-tetrabromide is converted by fuming nitric acid into ordinary dibromosuccinic acid. Tetrabromofurfurane is oxidised by boiling dilute nitric acid or bromine-water with production of dibromomaleic acid (m. p.  $123-125^\circ$ ).

*Tetrabromofurfurane dibromide*,  $C_4H_2Br_4O$ , obtained by the addition of bromine to tetrabromofurfurane, crystallises in six-sided scales melting at  $122-123^\circ$ ; it dissolves readily in ether or chloroform, less so in

alcohol and benzene, and is sparingly soluble in light petroleum or carbon bisulphide. It is gradually decomposed by boiling water, dibromomaleic acid being formed, whilst some bromine is set free.

A. K. M.

**Constitution of Thiophen Compounds.** By V. MEYER (*Ber.*, **18**, 526—529).—A discussion of the evidence in favour of the author's thiophen formula, and of the researches most likely to finally prove its correctness or incorrectness.

L. T. T.

**Synthesis of Thiophen.** By J. VOLHARD and H. ERDMANN (*Ber.*, **18**, 454—455).—When a mixture of succinic anhydride and phosphorus pentasulphide is heated at 140°, a violent action sets in with evolution of hydrogen sulphide. The distillate is agitated with soda solution, digested with sodium and fractioned; the product boiling at 83—84° is identical with coal-tar thiophen. A much better yield (half that required by theory) is obtained on distilling sodium succinate with phosphorus trisulphide. Thiosuccinyl and potassium thiosuccinate also yield thiophen when heated with phosphorus trisulphide. A thiotolen has also been produced in the same way from sodium pyrotartrate; it has the same boiling point as coal-tar thiotolen, from which it appears however to be distinct. The *tribromo*-derivative forms magnificent colourless needles melting at 34°, whilst the corresponding compound from coal-tar thiotolen melts at 74° (*Abstr.*, **1884**, 1132).

Thiophen is found to crystallise when cooled by a mixture of solid carbonic anhydride and ether, whilst methylthiophen remains almost entirely liquid, the small separation being probably due to impurity.

By the action of phosphorus trisulphide on sodium phthalate, a minute quantity of a solid substance is obtained which resembles naphthalene in its odour, and yields a greenish-blue coloration with isatin and sulphuric acid; a rather larger amount is obtained from sodium hydrophthalate.

A. K. M.

**Method of obtaining Thiophen and its Homologues.** By K. E. SCHULZE (*Ber.*, **18**, 497—498).—The author has previously shown that thiotolen and thioxylen can be obtained by passing steam through the sulphuric acid employed in purifying toluene and xylene. Thiophen may likewise be obtained from the acid used in the purification of benzene, but in this case the acid must be diluted with an equal bulk of water immediately after it is separated from the benzene, and then at once steamed. The amount of oil obtained is about 3.5 per cent. by volume of the acid taken, and this oil contains about 83 per cent. of pure thiophen; xylene and trimethylbenzenes are also present. If a larger proportion of water (2—3 vols.) be added to the sulphuric acid before steaming, the proportion of crude thiophen is the same, but it is of greater purity.

A. K. M.

**Thiophen from Erythrite.** By C. PAAL and J. TAFEL (*Ber.*, **18**, 688—689).—Thiophen is obtained in an impure state by distilling a mixture of erythrite, phosphorus pentasulphide, and sand.

A. J. G.



**Thiophen from Mucic Acid.** By C. PAAL and J. TAFEL (*Ber.*, **18**, 456—460).—An intimate mixture of mucic acid with twice its weight of barium sulphide is heated in a closed tube for six hours at 200—210°. The product is boiled three or four times with water, and the solution which contains barium thiophenate is filtered from the pulverulent residue (believed to contain thiophendicarboxylic acid). The *thiophenic acid* thus produced is very probably the  $\alpha$ -acid. It crystallises from water in long slender needles melting at 126—127°, is very readily soluble in ether, alcohol, and hot water; moderately soluble in chloroform, and sparingly in light petroleum. Its properties and reactions show it to be identical with the acid obtained by Nahnsen from iodothiophen (this vol., p. 51). On distilling the calcium salt from the crude acid with an excess of lime and purifying the distillate, 40 per cent. of the theoretical quantity of pure thiophen boiling at 83—84° is obtained, agreeing in all its properties with coal-tar thiophen. A. K. M.

**Nitrothiophens.** By O. STADLER (*Ber.*, **18**, 530—536).—This is a continuation of the author's previous work with V. Meyer (this vol., pp. 141 and 250). The dinitrothiophen melting at 52° previously described, is converted by repeated distillation into an *isomeric dinitrothiophen* melting at 78°. This latter compound crystallises in pale yellow prismatic needles, and is soluble in alcohol. It closely resembles its isomeride in properties. Both isomerides when heated with bromine at 180—200° yield tetrabromothiophen. The crystals of both isomerides belong to the monosymmetric system: those of the compound melting at 52° gave the measurements  $a : b : c = 0.755 : 1 : 0.568$ , and  $\beta = 59^\circ 28'$ ; those of the compound melting at 78°,  $a : b : c = 1.606 : 1 : 1.908$  and  $\beta = 74^\circ 21\frac{1}{2}'$ . The red coloration previously described as caused by the action of potash on the lower melting dinitrothiophen is so intense as to be plainly visible when only 0.0000001 gram of substance is present.

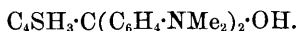
*Mononitrothiophensulphonic acid*,  $\text{NO}_2 \cdot \text{C}_4\text{SH}_2 \cdot \text{SO}_3\text{H}$ , forms white hygroscopic crystals which are reconverted into mononitrothiophen when heated. The *potassium*, *barium*, *calcium*, and *silver salts* are described. The *sulphochloride*,  $\text{NO}_2 \cdot \text{C}_4\text{SH}_2 \cdot \text{SO}_2\text{Cl}$ , is a thick oil having the characteristic odour of sulphochlorides. The *sulphonamide*,  $\text{NO}_2 \cdot \text{C}_4\text{SH}_2 \cdot \text{SO}_2\text{NH}_2$ , obtained by heating the sulphochloride with ammonium carbonate, crystallises in white needles melting at 172—173° (uncorr.). The crystals of mononitrothiophen belong to the monosymmetric system. L. T. T.

**$\beta$ -Acetothiënone and its Derivatives.** By A. PETER (*Ber.*, **18**, 537—542).—When completely oxidised,  $\beta$ -acetothiënone yields  $\beta$ -thiophenic acid (this vol., p. 141, and next Abstract), but when it is carefully treated with a cold dilute alkaline solution of potassium permanganate, the intermediate product  *$\beta$ -thiënylglyoxylic acid*,



is formed. This crystalline acid melts at 86°, and is soluble in water and ether. With benzene containing thiophen and concentrated sul-

phuric acid, it yields a red colouring matter analogous to that obtained by Claisen from phenylglyoxylic acid and impure benzene. With strong sulphuric and acetic acids, a brown coloration is first produced, which then changes to bluish-green, dark green, violet, red, bluish-violet, and finally blue. When heated in an atmosphere of hydrogen, this acid yields  $\beta$ -thiophenaldehyde,  $C_4SH_3 \cdot COH$ , a yellowish oil having an odour recalling both benzaldehyde and furfuraldehyde. When heated with dimethylaniline and zinc chloride, a green colouring matter resembling malachite-green is formed, which the author calls *thiophen-green*. It dyes silk a yellow shade of green. On reduction, this colouring matter yields a *leuco-base*, and alkalis precipitate from its acid solutions a reddish-coloured substance which the author believes to be *tetramethyldiamido-diphenylthiënylcarbinol*,



*Isonitrosothiënylacetic acid*,  $C_4SH_3 \cdot C(NO_2) \cdot COOH$ , prepared from the above acid and hydroxylamine, forms white needles melting at  $136^\circ$ . *Monochloro- $\beta$ -acetothiënone*,  $C_4SH_3 \cdot CO \cdot CH_2 \cdot Cl$ , obtained by passing chlorine into the vapour of boiling acetothiënone, forms white crystals. It melts at  $47^\circ$  and boils at  $259^\circ$  (corr.). When oxidised, it yields  $\beta$ -thiophenic acid. *Dinitro- $\beta$ -acetothiënone*,  $C_4SH(NO_2)_2 \cdot COMe$ , obtained from either of the mononitro-derivatives already described (this vol., p. 141), melts at  $166$ – $167^\circ$ . Mononitroacetothiënone of melting point  $122.5$ , when oxidised with nitric acid of sp. gr.  $1.15$ , yields *nitro- $\beta$ -thiënylglyoxylic acid*,  $NO_2 \cdot C_4SH_2 \cdot CO \cdot COOH$ , a yellowish crystalline substance melting at  $92^\circ$ . The mononitro-acetothiënone melting at  $86^\circ$  gives an analogous acid.

L. T. T.

#### Isomeric Thiophenic Acids. By A. PETER (*Ber.*, **18**, 542–544).

—The thiophenic acid obtained by the author by the oxidation of acetothiënone and melting at  $124.5$  (this vol., p. 142) has proved to be Nahnsen's  $\beta$ -thiophenic acid, melting at  $126^\circ$  (this vol., p. 51). The author has also prepared some derivatives of  $\alpha$ -thiophenic acid melting at  $118^\circ$ .  *$\alpha$ -Thiophenic chloride* boils at  $206^\circ$  (uncorr.);  *$\alpha$ -thiophenamide*,  $C_4SH_3 \cdot CONH_2$ , crystallises in needles, soluble in water and ether, and melting at  $171.5$ ; *dibromo- $\alpha$ -thiophenic acid* crystallises in short white needles melting at  $209$ – $211^\circ$ .

L. T. T.

#### Isomeric Thiophensulphonic Acids. By J. LANGER (*Ber.*, **18**,

553–563).—A continuation of the author's previous communication on this subject (*Abstr.*, 1884, 1133). *Dibromo- $\beta$ -thiophensulphonamide*,  $C_4SBr_2H \cdot SO_2NH_2$ , crystallises in colourless needles melting at  $146.5$ – $147^\circ$ . The *chloride*,  $C_4SBr_2H \cdot SO_2Cl$ , is a yellowish oil.  *$\beta$ -Thiophensulphonic acid*,  $C_4SH_3 \cdot SO_3H$ , obtained by boiling its chloride with water, is a white crystalline and highly hygroscopic substance of strongly acid character, and is easily soluble in water. When heated with isatin and strong sulphuric acid, it gives a bright blue coloration. The *barium salt* forms small white crystals, moderately soluble in cold, freely in hot water. *Dibromo- $\beta$ -thiophendisulphonic acid*, obtained from its anhydride, was debrominated by treating a concentrated solution of its sodium salt with sodium-amalgam.  *$\beta$ -Thiophen-*

*disulphonic acid* is a white crystalline substance easily soluble in water. The *chloride*,  $C_4SH_2(SO_2Cl)_2$ , crystallises in white scales melting at  $148-149^\circ$  with decomposition. It is easily soluble in ether, and has the characteristic odour of sulphonie chlorides. It is isomeric with the compound melting at  $70^\circ$ , which Jaekel obtained by the direct sulphonation of thiophen.  $\beta$ -*Thiophendisulphonamide* crystallises in white needles, sparingly soluble in cold water. It begins to blacken at  $240^\circ$ , and melts with decomposition above  $280^\circ$ . *Dibromo- $\beta$ -thiophendisulphonic chloride* forms silky white needles melting with decomposition at  $215^\circ$ ; it is moderately soluble in ether and water. The *sulphonamide*,  $C_4SBr_2(SO_2NH_2)_2$ , forms a white powder, very sparingly soluble in boiling water, and melts with partial decomposition above  $270^\circ$ . The *lead*, *sodium*, and *ammonium* salts are described.

The sulphonation of moniodothiophen is very difficult, as resinification sets in very easily. But by carefully treating small quantities of iodothiophen, dissolved in light petroleum, with fuming sulphuric acid, the author obtained an *iodothiophendisulphonic acid*, which, however, could not be isolated. It was therefore at once de-iodated, and then yielded an acid from which a *thiophendisulphonamide*,



was obtained. This crystallises in scales, melting at  $142^\circ$ , and is therefore quite distinct from its two isomerides already described by the author and by Jaekel respectively. It is easily soluble in boiling water; with isatin and sulphuric acid, it gives a deep violet-blue coloration. In the sulphonation of iodothiophen, the author sometimes obtained an *iodothiophenmonosulphonic acid* which, when de-iodated, yielded  $\beta$ -*thiophensulphonic acid*.  
L. T. T.

**Isomeric Thiotolens (Methylthiophens).** By K. EGLI (*Ber.*, 18, 544—549).—The author finds that the natural and synthetical thiotolens obtained by V. Meyer and H. Kreis (Abstr., 1884, 1131 and 1132) are isomeric and not identical. Thiotolen from coal-tar yields  $\alpha$ -thiophenic acid when oxidised, whereas synthetical ethylthiophen (and therefore synthetical thiotolen) gives  $\beta$ -thiophenic acid. The natural product is therefore  $\alpha$ -*thiotolen* (probably S : Me = 1 : 2), the synthetical  $\beta$ -*thiotolen* (probably S : Me = 1 : 3).  $\beta$ -Thiotolen yields *tribromo- $\beta$ -thiotolen*, crystallising in long, colourless, silky needles, melting at  $86^\circ$ , and easily soluble in ether and boiling alcohol. The corresponding  $\alpha$ -derivative, melting at  $74^\circ$ , has already been obtained by Meyer and Kreis (*loc. cit.*).  
L. T. T.

**Derivatives of  $\beta$ -Ethylthiophen.** By R. BONZ (*Ber.*, 18, 549—552).—*Tribromo- $\beta$ -ethylthiophen*,  $C_4SBr_3Et$ , crystallises in white scales melting at  $108^\circ$ . It dissolves sparingly in cold alcohol or ether, more easily on boiling. The substitution takes place only in the thiophen nucleus, whereas in the isomeric  $\alpha$ -ethylthiophen (thioxylene from coal-tar) the whole of the hydrogen may, according to Messinger, be replaced by bromine. *Dibromo- $\beta$ -ethylthiophen*,  $C_4SHBr_2Et$ , obtained by gradually adding the theoretical quantity of bromine to a solution of  $\beta$ -ethylthiophen in glacial acetic acid, is an oil of peculiar

odour. *Dichloro-β-ethylthiophen*,  $C_4SHCl_2Et$ , is a pale yellow oil boiling at  $235-237^\circ$  (corr.); no more highly chlorinated derivatives could be isolated. *Moniodo-β-ethylthiophen* is a light yellow oil; no di-iodo-derivative was obtained. *Dinitro-β-ethylthiophen*,



was prepared by passing a stream of air saturated with  $\beta$ -ethylthiophen through fuming nitric acid; it is a yellowish oil, and its alcoholic solution when treated with a few drops of alkali gives an intense blue coloration.

L. T. T.

**Thioxylen from Coal-tar.** By J. MESSINGER (*Ber.*, **18**, 563—568).—The author has investigated the crude thioxylen obtained by Schulze (this vol., p. 251) from the acid used in purifying xylene. *Dibromothioxylen*,  $C_4SBr_2Me_2$ , was obtained by slowly adding bromine to well cooled thioxylen, and boiling the product with alcoholic potash to decompose the bromo-additive products formed; it crystallises in long colourless needles, melts at  $46^\circ$ , and boils at  $246-247^\circ$  (uncorr.). *Octobromothioxylen*,  $C_4SBr_2(CBr_3)_2$ , prepared by treating dibromothioxylen with bromine as long as any reaction takes place, crystallises in small yellowish needles melting at  $114^\circ$ , and decomposing a few degrees above that temperature. *Thioxylen*,  $C_4SH_2Me_2$ , was isolated from the crude product mentioned above by V. Meyer and H. Kreis's method (*Abstr.*, 1884, 1132), and the mixture of xylene and iodothioxylen obtained fractioned in a current of steam. Thus purified, thioxylen is a clear, colourless, and mobile liquid of not unpleasant odour, boiling at  $136.5-137.5^\circ$  (uncorr.). It gives Laubenheimer's reaction, and when oxidised with alkaline potassium permanganate yields *thiophendicarboxylic acid*,  $C_4SH_2(COOH)_2$ . This acid forms a snow-white powder, very sparingly soluble in water, more easily in ether. When heated to  $350^\circ$ , it sublims without fusion, but can be melted by heating quickly in the direct flame in a capillary tube. *Methyl thiophendicarboxylate* crystallises in glittering white needles, only moderately soluble in ether, and melting at  $142^\circ$ . The character of the methyl salt seems to point to the acid corresponding with terephthalic acid, but the properties of the free acid are more like those of isophthalic acid.

L. T. T.

**Influence of Light on the Action of Halogens on Aromatic Compounds.** By J. SCHRAMM (*Ber.*, **18**, 606—608).—When bromine is allowed to act on benzene in equal molecular proportions light seems to have no influence on the reaction. The time of reaction is about the same whether the experiment is carried out in the dark, in diffused daylight, or in direct sunlight. The addition of iodine, even in very small proportion, intensifies the reaction very much. In all cases monobromobenzene is formed. The case is different with toluene. In the dark and in diffused daylight a mixture of ortho- or para-bromotoluene is formed, but in direct sunlight the substitution takes place exclusively in the side group, benzyl bromide being formed. The reaction is very energetic, but the end product is the same whether the temperature of the toluene is allowed to rise or is kept at  $0^\circ$  by cooling. The addition of iodine causes the

substitution to take place in the benzene nucleus. Chlorine acts in precisely the same way, and, if in direct sunlight, the quantity of chlorine be increased, benzyldene chloride and benzotrichloride are formed. Preliminary experiments on the action of bromine on the xylenes seems to show that here also substitution takes place in the side-groups in direct sunlight.

L. T. T.

**Action of Aluminium Chloride on Mixtures of Ethylidene Chloride with Benzene, Toluene, or Metaxylene.** By R. ANSCHÜTZ and E. ROMIG (*Ber.*, **18**, 662—666).—Anschütz and Angelbis, by heating a mixture of ethylidene chloride, benzene, and aluminium chloride, obtained a substance which they described as dimethylantracene hydride (*Abstr.*, 1884, 753). As in a recent communication (*Ann. Chim. Phys.* [6], **1**, 485), Friedel and Crafts seem to regard this compound as dimethylantracene, an experimental proof of its composition appeared necessary, and was obtained in the formation of the solid dibromide,  $C_{18}H_{14}Br_2$ . This compound would be formed from dimethylantracene by the direct addition of one molecule of bromine, whilst if formed by the replacement of hydrogen in dimethylantracenehydride, 2 mols. of bromine would be required, and hydrogen bromide would be found as a product of the action; the latter supposition was found to be correct.

By the action of nitric acid on a solution of diphenylethane in glacial acetic acid there were obtained *nitrodiphenylethane*,



crystallising in long yellow needles, melting at  $79-80^\circ$ , *dinitrodiphenylethane*,  $CHMe(C_6H_4NO_2)_2$ , crystallising in prismatic needles, melting at  $149^\circ$ , and more sparingly soluble in alcohol than the mononitro-compound, and *nitrodiphenylmethylcarbinol*,



forming colourless prismatic crystals, and melting at  $106-107^\circ$ . When heated with acetic chloride, the carbinol is converted into *nitrodiphenylethylene*,  $NO_2 \cdot C_6H_4 \cdot CPh : CH_2$ , forming compact crystals, and melting at  $86^\circ$ .

*Tetramethylantracene hydride*,  $C_6H_3Me < \begin{smallmatrix} CHMe \\ CHMe \end{smallmatrix} > C_6H_3Me$ , is obtained together with ditolyethane and paramethylethylbenzene, by heating a mixture of toluene, ethylidene chloride, and aluminium chloride. It crystallises in tables, melts at  $171-171.5^\circ$ , and is readily soluble in benzene. When treated with bromine, it yields hydrogen bromide and a dibromide,  $C_{18}H_{16}Br_2$ , sparingly soluble in glacial acetic acid. The picrate,  $C_{18}H_{20} \cdot C_6H_2(NO_2)_3 \cdot OH$ , forms brownish-red needles, melting at  $165^\circ$ . Both the hydrocarbon and the dibromide when oxidised with chromic acid yield a *dimethylantracenequinone*,  $C_6H_3Me < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C_6H_3Me$ , melting at  $236^\circ$ , and sparingly soluble in alcohol and glacial acetic acid. When treated with zinc-dust and aqueous potash, tetramethylantracene yields a hydrocarbon melting at  $243-244^\circ$ , probably a dimethylantracene.

*Ditolylethane*,  $\text{CHMe}(\text{C}_6\text{H}_4\text{Me})_2$ , is the main product of the above reaction; it is a liquid, shows a blue fluorescence, boils at  $153\text{--}156^\circ$  under 11 mm., and at  $294\text{--}295^\circ$  under the ordinary pressure. When oxidised with potassium permanganate in acid solution, it yields toluybenzoic acid, melting at  $222^\circ$ , and a benzophenondicarboxylic acid. It is probably identical with Fischer's dimethyldiphenylethane (this Jour., 1875, 155).

*Paramethylethylbenzene*,  $\text{C}_6\text{H}_4\text{MeEt}$ , prepared as above mentioned, is a colourless liquid; it boils at  $161\text{--}163^\circ$ , and is completely converted into terephthalic acid.

*Diarylethane*,  $\text{CHMe}(\text{C}_6\text{H}_3\text{Me}_2)_2$ , is formed together with a dimethylethylbenzene by the action of aluminium chloride on a mixture of ethylidene chloride and metaxylene; no compound of the anthracene series could be isolated from the product of this reaction. It is a strongly refractive liquid, boiling at  $169\text{--}172^\circ$  under 11 mm. pressure. The *dimethylethylbenzene*,  $\text{C}_6\text{H}_3\text{Me}_2\text{Et}$ , formed, boils at  $186^\circ$ , and yields nitric acid on oxidation. A. J. G.

**Preparation of Homologues of Benzene by Aid of Aluminium Chloride.** By R. ANSCHÜTZ and H. IMMENDORFF (*Ber.*, 18, 657—662).—As the result of their researches on the reversal of Friedel and Crafts' reaction and the transference of the side-chains from one position to another (comp. Friedel and Crafts, *Trans.*, 1882, 116; Jacobsen, this vol., p. 516), the authors give the following:—

Toluene is converted on the one hand into benzene, on the other into paraxylene and metaxylene, the latter being the main product.

Metaxylene by elimination of methyl-groups yields toluene and benzene, and by addition, or by successive elimination and addition gives paraxylene, pseudocumene, mesitylene, durene, and isodurene. Orthoxylene is not formed.

Pseudocumene yields the same products as metaxylene, only in different proportions.

Ethylbenzene yields benzene, much paradiethylbenzene, and but little metadiethylbenzene.

A considerable quantity of toluene is formed by the action of aluminium chloride on cymene. A. J. G.

**Trichlorotoluenes.** By E. SEELIG (*Ber.*, 18, 420—426). When trichlorotoluene is fractioned five or six times, and the portion distilling between  $228\text{--}235^\circ$  fractionally crystallised from methyl alcohol, it is found to contain not only  $\alpha$ -trichlorotoluene, melting at  $82^\circ$  and boiling at  $229\text{--}230^\circ$  (*Annalen*, 139, 326; 146, 325; 187, 274), but also a  $\beta$ -trichlorotoluene, melting at  $41^\circ$  and boiling at  $231\text{--}232^\circ$ . A better separation may be effected by treating the crude product with fuming sulphuric acid, with which the  $\beta$ -compound alone readily forms sulphonic acids. The unaltered  $\alpha$ -trichlorotoluene is then expelled by steam, and the  $\beta$ -derivative subsequently recovered by hydrolysis (*Trans.*, 1884, 148). By the further chlorination of trichlorotoluene, a carbonaceous product is obtained, containing principally pentachloro-, and only a little tetrachloro-toluene. The following nitro- and amido-trichlorotoluenes are described:  $\alpha$ -mononitro-

*trichlorotoluene*, forming colourless scales, melting at  $92^{\circ}$ , and  $\beta$ -*mononitrotrichlorotoluene*, long, yellowish needles, melting at  $60^{\circ}$ ; the  $\alpha$ -*dinitro*-derivative crystallises in colourless scales or needles, melting at  $227^{\circ}$ , whilst the  $\beta$ -*dinitro*-compound forms yellowish-white needles, melting at  $141^{\circ}$ ;  $\alpha$ -*trichlorotoluylenediamine* forms white acicular crystals, melting at  $196^{\circ}$ , whilst the trichloro- $\beta$ -*diamine* melts at temperatures varying from  $195^{\circ}$  to  $207^{\circ}$ ;  $\alpha$ -*trichlorotoluidine* crystallises in needles melting at  $94$ – $95^{\circ}$ , and  $\beta$ -*trichlorotoluidine* in slender dirty-white needles melting at  $105^{\circ}$ . By the action of alcoholic ammonia on the dinitro-compounds at  $80$ – $100^{\circ}$ , *amidonitrotrichlorotoluenes* are produced, the  $\alpha$ -derivative crystallising in orange-yellow needles melting at  $191^{\circ}$ , and the  $\beta$ -derivative in orange-red needles melting at  $192^{\circ}$ . When the  $\alpha$ -diamine is boiled for six hours with an excess of acetic anhydride, a tetracetyl derivative, melting at  $220^{\circ}$ , is obtained, whilst on boiling the  $\beta$ -diamine for 40–50 hours with glacial acetic acid an anhydro-base melting at about  $300^{\circ}$  is produced, showing that the  $\beta$ -compound is an orthodiamine. The readiness with which the  $\alpha$ -diamine may be converted into trichlorotoluquinone (this Jour., 1874, 61 and 1095), indicates that the chlorine-atoms in  $\alpha$ -trichlorotoluene occupy the positions [2:4:5], and that the two hydrogen atoms are in the para-position. Both  $\alpha$ - and  $\beta$ -trichlorotoluenes are produced on chlorinating para- and ortho-chlorotoluenes, proving that the chlorine-atoms in the  $\beta$ -compound occupy the positions [2:3:4]. When chlorine is passed into boiling trichlorotoluene, not only is Beilstein and Kuhlberg's liquid  $\alpha$ -trichlorobenzal chloride (b. p.  $280$ – $281^{\circ}$ , *Annalen*, **150**, 299) produced, but also a crystalline  $\beta$ -trichlorobenzal chloride melting at  $84^{\circ}$ ; both yield crystalline and moderately stable aldehydes,  $\alpha$ -trichlorobenzaldehyde melting at  $112$ – $113^{\circ}$ , and the  $\beta$ -aldehyde at  $90^{\circ}$ . By the oxidation of the latter with potassium permanganate, it yields  $\beta$ -trichlorobenzoic acid melting at  $129^{\circ}$ , whilst on heating it with acetic anhydride and sodium acetate,  $\beta$ -trichlorocinnamic acid melting at  $185^{\circ}$ , and  $\alpha$ -trichlorocinnamic acid melting at  $200$ – $201^{\circ}$ , are obtained.

A. K. M.

**Reduction of Nitrobenzyl Chloride.** By G. PELLIZZARI (*Gazzetta*, **14**, 481–483).—With a view of obtaining nitro-derivatives of the benzylic ethers of the dihydroxybenzenes described by the author (Abstr., 1884, 437), nitrobenzyl chloride was heated with the hydroxybenzenes in the presence of potash. With quinol and resorcinol, however, the product of the reaction was the nitrotoluene melting at  $54^{\circ}$  and distilling at  $236^{\circ}$  without decomposition. In the case of pyrogallol, the formation of nitrotoluene may be effected even in aqueous solution. This result may be explained by supposing that the nitrobenzyl ether at first formed in the presence of the alkali, is decomposed into nitrotoluene and nitrobenzoic acid, precisely as benzyl alcohol is converted into toluene and benzoic acid. If this were a reasonable explanation, then it is probable that a more oxidisable substance, such as pyrogallol, would the more readily form nitrotoluene than the less oxidisable substances, quinol and resorcinol. As an evidence of this hypothesis, it is noted that gallic and digallic acid, highly oxidisable

substances, are converted into nitrotoluene, although not the slightest trace can be obtained from salicylic acid. V. H. V.

**Paranitrobenzylidene Chloride.** By J. ZIMMERMANN and A. MÜLLER (*Ber.*, 18, 996—997).—The preparation of this compound has been frequently attempted. According to Meister, Lucius, and Brünning's patent, it is obtained by chlorinating paranitrotoluene at 130—160°. The authors, however, have failed to obtain it by this method, although they carefully observed the conditions described in the patent; the product consists of an oil which has not been identified, and of a solid, which is principally paranitrobenzoic acid, but also contains paranitrobenzyl chloride. Paranitrobenzylidene chloride may, however, be obtained by the action of phosphorus pentachloride on paranitrobenzaldehyde; the latter is gradually added to twice its weight of the pentachloride, and the mixture heated for a short time on the water-bath. On pouring the product, when cold, into iced water, an oil separates, which at once crystallises. Paranitrobenzylidene chloride is readily soluble in alcohol and ether, insoluble in water; it crystallises in nearly colourless, short, well-formed prisms, melting at 46°. When its alcoholic solution is boiled with silver nitrate, silver chloride separates. By the action of concentrated sulphuric acid or by continued boiling with water, paranitrobenzaldehyde is reproduced.

The action of aniline on paranitrobenzylidene chloride yields the same result as the corresponding bromide (this vol., p. 386).

An attempt to prepare orthonitrobenzylidene chloride from orthonitrobenzaldehyde and phosphorous pentachloride, yielded a substance insoluble in alcohol and ether. A. K. M.

**1 : 3 : 4 : 5 Nitropseudocumene, Pseudocumidine, and Pseudocumenol.** By E. EDLER (*Ber.*, 18, 629—630).—The derivatives of pseudocumene previously known belong to the symmetrical [1 : 3 : 4 : 6] series. In order to prepare a second series, ordinary pseudocumidine was acetylated and nitrated, and the acetyl- and amido-groups then removed in the usual manner. The isomeric nitropseudocumene thus obtained was converted into the corresponding pseudocumidine and pseudocumenol.

*Acetopseudocumide*,  $C_6H_2Me_3 \cdot NH\bar{A}c$  [ $Me_3 : NH\bar{A}c = 1 : 3 : 4 : 6$ ], crystallises in white needles, melts at 161°, and is moderately soluble in hot alcohol. Its *nitro*-derivative,  $NO_2 \cdot C_6HMe_3 \cdot NH\bar{A}c$  [ $NO_2 = 5$ ], forms pale-yellow prisms, melts at 193—194°, is soluble in alcohol, but nearly insoluble in ether. *Nitropseudocumidine*,  $NO_2 \cdot C_6HMe_3 \cdot NH_2$  [ $Me_3 : NO_2 : NH_2 = 1 : 3 : 4 : 5 : 6$ ], crystallises in red triclinic needles, melts at 46—47°, and is soluble in alcohol and ether.

*Nitropseudocumene*,  $C_6H_2Me_3 \cdot NO_2$  [ $= 1 : 3 : 4 : 5$ ], distils with steam as a pale-yellow oil, solidifying to large thick prisms; it melts at 20°.

*Pseudocumidine*,  $C_6H_2Me_3 \cdot NH_2$  [ $= 1 : 3 : 4 : 5$ ], forms a colourless crystalline mass, melts at 36°, and distils readily with steam. The *nitrate* crystallises in small lustrous plates, and is much more soluble than that of symmetrical pseudocumidine. The *hydrochloride* crystallises in slender interlaced needles; the *sulphate* in short anhydrous



prisms, sparingly soluble in cold water, and the oxalate in large colourless plates. 1 : 3 : 4 : 5 *Pseudocumenol*,  $C_6H_2Me_3\cdot OH$ , melts at  $93^\circ$ ; its *dibromo*-derivative,  $C_6Me_3Br_2\cdot OH$ , crystallises in long needles and melts at  $148$ — $149^\circ$ .

Proof that the nitro-group occupies the position adjacent to the amido-group in nitropseudocumidine was given by the products of the reduction both of the base and its acetyl-derivative. Acetopseudocumide, when treated with zinc and acetic acid, yielded a condensation product of the formula  $C_6HMe_3\text{--}\begin{smallmatrix} NH \\ \diagup \quad \diagdown \\ - \quad N \end{smallmatrix}\text{--}CMe$ , from which the acetyl nucleus could not be removed by prolonged boiling with potash. In like manner, the pseudocumylenediamine,  $C_6HMe_3(NH_2)_2$ , obtained by reducing nitropseudocumidine, showed the properties of an orthodiamine. It crystallises in colourless plates, melts at  $90^\circ$ , is readily soluble in alcohol and ether, and moderately in hot water. The dilute solution of its hydrochloride gives an intense red coloration with ferric chloride. A solution of the base in dilute sulphuric acid gives a pale-brown coloration with sodium nitrite. The dry hydrochloride, when heated on the water-bath with benzaldehyde, gives off hydrogen chloride (compare Ladenburg, *Abstr.*, 1878, 571, and 1879, 232).

A. J. G.

**$\alpha$ -Phenylpropylene and  $\alpha$ -Paratolylpropylene.** By G. ERRERA (*Gazzetta*, 14, 504—510).—In a former memoir (p. 654) the author described an unsaturated hydrocarbon, allylmethylbenzene,



or paratolylpropylene, obtained by the action of alcoholic potash on monochlorocymene. In order to decide between the two possible formulæ  $C_6H_4Me\cdot CH:CHMe$  and  $C_6H_4Me\cdot CH_2\cdot CH:CH_2$ , the hydrocarbon was treated with hydrobromic acid, but the result was a polymeric modification, probably  $[C_6H_4Me\cdot C_3H_5]_2$ , which is partially decomposed at the boiling point of sulphur. As this process failed in its object, the problem was solved by the analogy of the reactions of allylbenzene,  $C_6H_5\cdot C_3H_5$ , obtained by decomposing monochloropropylbenzene with alcoholic potash. This substance, boiling at  $178^\circ$ , is identical with the hydrocarbon obtained by Perkin and Fittig; it readily takes up 1 mol. Br to form a dibromopropylbenzene, crystallising in white glistening needles, which is decomposed on distillation, yielding an allylbenzene or  $\alpha$ -phenylpropylene, boiling at  $168^\circ$ . The latter is transformable into a polymeric modification, boiling at  $33^\circ$ , and soluble in ether and alcohol. As the constitution of this  $\alpha$ -phenylpropylene is probably represented by the formula  $C_6H_5\cdot CH:CHMe$ , being obtained from a hydrocarbon,  $C_6H_5\cdot CH_2\cdot CH:CH_2$ , and as it is analogous to the  $\alpha$ -paratolylpropylene in yielding a polymeric modification, then the constitution of the latter is probably represented by the formula  $C_6H_4Me\cdot CH:CHMe$ , and its polymeride,  $(C_6H_4Me\cdot CH:CHMe)_2$ , corresponds with Berthelot's metastyrolene.

V. H. V.

**Nitriles from Aromatic Formamides.** By K. GASIOROWSKI and V. MERZ (*Ber.*, 18, 1001—1014).—When formanilide is boiled in a reflux apparatus, a carbylamine odour manifests itself, but after-

wards disappears, whilst the boiling point sinks from  $278^{\circ}$  to  $234^{\circ}$ . On then distilling the product, a distillate is obtained containing aniline, apparently accompanied by a trace of benzonitrile, also methenyldiphenylamine. If formanilide be boiled with an excess of zinc-dust, the odour of phenylcarbylamine first appears and then gives place to that of benzonitrile, whilst hydrogen mixed with carbon monoxide and carbonic anhydride is evolved. On distilling the product, aniline and benzonitrile, boiling at  $192$ — $194^{\circ}$ , are obtained. The operation should be conducted in an atmosphere of hydrogen. A part of the aniline is most probably produced by the direct elimination of carbon monoxide from formanilide. The yield of nitrile amounts to from 10 to nearly 20 per cent. of the weight of the formanilide.

Similar results are obtained on heating formyl-ortho- and para-toluides with zinc-dust, the yield of nitrile amounting to 15—20 per cent. of the substance taken. Formyl- $\alpha$ - and formyl- $\beta$ -naphthalides likewise yield 10—12 per cent. of their weight of  $\alpha$ - and  $\beta$ -naphthonitrile. Isobutylformanilide,  $C_4H_9 \cdot C_6H_4 \cdot NH \cdot CHO$ , obtained by heating amidoisobutylbenzene for several hours with an excess of strong formic acid, melts at  $59^{\circ}$ , is sparingly soluble in cold, readily in warm light petroleum, in alcohol, and in ether, almost insoluble in cold, sparingly in warm water. It yields isobutylbenzonitrile (12 per cent.) when heated with zinc-dust. Formylmetaxylide (melting at  $113$ — $114^{\circ}$ ) also yields metaxylonitrile (12 per cent.), which on hydrolysis is converted into ordinary xylic acid (m. p.  $126^{\circ}$ ).

Effront obtained two isomeric isobutylorthotolunitriles by heating the corresponding formotoluides with zinc-dust (this vol., p. 153), and Beran likewise prepared parocetylbenzonitrile from parocetylformanilide.

Formylbenzidine, on the other hand, did not yield the corresponding nitrile.

A. K. M.

**Reactions of Aromatic Cyanates.** By R. LEUCKART (*Ber.*, **18**, 873—877).—Phenyl cyanate reacts with benzene in presence of aluminium chloride, forming *benzanilide*,  $PhCO \cdot NHPh$ , melting at  $159^{\circ}$ . Paratoluy cyanate and naphthyl cyanate react in a manner analogous to phenyl cyanate. The reaction appears to take place in two phases, in the first of which by the union of hydrochloric acid and phenyl cyanate, *phenylcarbamic chloride*,  $ClCO \cdot NHPh$ , is formed, and this, reacting with benzene, forms benzanilide and hydrochloric acid.

All true homologues of benzene react in a similar manner with phenyl cyanate and aluminium chloride, the group  $CONHPh$  usually taking the para-position; the existence of a side-chain in this position does not appear to interfere with the reaction. Derivatives of the hydrocarbons containing electronegative elements or radicles do not react with phenyl cyanate. The reaction of phenyl cyanate with phenols described by Hofmann (*Ber.*, **4**, 249) and recently by Gumpert (*Abstr.*, 1885, 656), takes place more easily and at lower temperatures in presence of aluminium chloride. By the reaction of phenetol with phenyl cyanate and aluminium chloride, a compound is formed which melts at  $163^{\circ}$ , and is volatile without decomposition.

The study of the action of phenyl cyanates on amines containing electronegative elements and radicles has shown that their presence merely affects the energy of the reaction, and this to a greater extent with ortho- and para- than with meta-derivatives, whilst the presence of two such groups prevents the action.

The action of phenyl cyanate on diamines is still being investigated.

P. P. B.

### Compounds of Polyhydric Alcohols with Phenyl Cyanate.

By H. TESSMER (*Ber.*, **18**, 968—972).—The *glyceride of phenylcarbamic acid*,  $C_3H_5(O\cdot CONHPh)_3$ , is obtained, when glycerol (1 mol.) and phenyl cyanate (3 mols.) are heated together; any unaltered phenyl cyanate is removed by means of dry ether or benzene and the glycerol with cold water, after which the product is crystallised from alcohol. It is soluble in chloroform, acetone, and ether, very sparingly in benzene and boiling water, and crystallises from alcohol in slender needles melting at  $160\text{--}180^\circ$ ; it is very stable, being only slightly decomposed by boiling with baryta-water or hydrochloric acid, but when heated at  $150^\circ$  with barium hydroxide and water, it is completely decomposed, barium carbonate, aniline, and glycerol being produced. The *erythride*,  $C_4H_6(O\cdot CONHPh)_4$ , is prepared in the same way as the glyceride, and forms a white, microcrystalline mass, sparingly soluble in benzene, ether, alcohol, acetone, and ethyl acetate; it softens at about  $210^\circ$ , and melts at  $215^\circ$  with decomposition. When heated with baryta, it splits up into carbonic anhydride, aniline, and erythrol. The *mannitol-derivative*,  $HO\cdot C_6H_8(O\cdot CONHPh)_5$ , closely resembles the erythride. It softens at  $250^\circ$ , melts at  $260^\circ$  with decomposition, and is decomposed when heated with baryta into carbonic anhydride, aniline, and mannitol. The *dulcitol-compound*,  $OH\cdot C_6H_8(O\cdot CONHPh)_5$ , is very sparingly soluble in all solvents, melts at about  $250^\circ$ , and is decomposed by baryta into carbonic anhydride, aniline, and dulcitol. The *quinovide*,  $C_6H_8O(O\cdot CONHPh)_3$  (?) is very soluble in cold alcohol.

Quercitol and saccharin. on the other hand, remain unaltered when boiled with phenyl cyanate. Grape-sugar yields diphenylcarbamide; phenyl isothiocyanate and glycerol yield diphenylthiocarbamide,  $CS(NHPh)_2$ .

A. K. M.

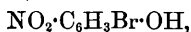
### Conversion of Phenyl Cyanate into Phenyl Cyanurate.

By A. W. HOFMANN (*Ber.*, **18**, 765—766).—The author has shown (*Annalen*, Supp. I, 57) that under the influence of triethylphosphine, phenyl cyanate is converted into phenyl dicyanate and not into a cyanurate, as was expected. The conversion into cyanurate is readily effected by heating with potassium acetate at  $100^\circ$ . The cyanurate formed is that modification previously obtained by the author from triphenylmelamine (*Ber.*, **3**, 260). It melts at  $270^\circ$ , not  $264^\circ$ , as previously stated. Phenyl cyanate boils constantly at  $166^\circ$  under a pressure of 769 mm.

A. J. G.

### Bromonitrophenols and their Amido-derivatives.

By J. LINDNER (*Ber.*, **18**, 611—615).—*Monobromometanitrophenol*,

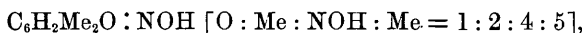


crystallises in long yellow needles easily soluble in alcohol, ether, and boiling water, and melting at  $147^{\circ}$ . With potassium carbonate, it yields the *potassium* derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{OK} + 2\text{H}_2\text{O}$ . The *barium* and *silver* derivatives are described. *Bromometanitrophenetol* (*bromonitrophenyl ethyl oxide*),  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{OEt}$ , crystallises in prisms melting at  $57^{\circ}$ . *Bromometamidophenyl ethyl oxide*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{OEt}$ , is a yellow oil insoluble in water, giving crystallisable salts with acids and with stannic chloride, &c. *Dibromometanitrophenol*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{OH}$ , crystallises in pale yellow scales melting at  $91^{\circ}$ , and very sparingly soluble in water. Its *potassium*, *barium*, and *silver* derivatives are described. Its *ethyl ether* forms pale yellow needles melting at  $110^{\circ}$ .

*Dibromometamidophenyl ethyl oxide*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{OEt}$ , is a yellow oil giving salts with acids, which crystallise in needles and are easily decomposed by water. *Tribromometanitrophenol*,  $\text{NO}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{OH}$ , forms almost colourless needles melting at  $85^{\circ}$ , and is very sparingly soluble in boiling water. Its *potassium*, *barium*, *silver*, and *ethyl* derivatives are described, the last-named melting at  $79^{\circ}$ . *Tribromometamidophenyl ethyl oxide* is a yellow solid forming crystallisable salt.

L. T. T.

**Nitrosophenols.** By H. GOLDSCHMIDT and H. SCHMID (*Ber.*, 18, 568—573).—In continuation of their previous work (Abstr., 1884, 1327), the authors describe the conversion of phlorone into nitroso-paraxylol. The phlorone used was prepared by oxidising amido-paraxylene with dilute chromic solution, and melted at  $123.5^{\circ}$ . When treated with hydroxylamine hydrochloride in slightly acid solution it yielded *phloroneoxime* (*nitroso-paraxylol*),



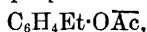
crystallising in pale yellow needles melting at  $163^{\circ}$ . Oliveri (Abstr., 1882, 837) gives the melting point as  $160\text{--}165^{\circ}$ . When oxidised with potassium ferricyanide in alkaline solution, it yields *nitroparaxylol* melting at  $122^{\circ}$  (Oliveri gives  $115^{\circ}$ ), and dissolves in alkali to a yellow solution. *Amidoparaxylol hydrochloride*, prepared by heating the nitro-compound with tin and hydrochloric acid, forms white crystals, and is readily oxidised to phlorone by dilute chromic solution. *Amidoparaxylol* crystallises in white scales which decompose at  $180^{\circ}$ .

As a further proof of the correctness of Goldschmidt's view of the nitrosophenols as naphthaquinoximes (Abstr., 1884, 1137), the authors have subjected these two isomerides to reduction.  $\beta$ -Nitroso- $\alpha$ -naphthol methyl ether gave  $\beta$ -amido- $\alpha$ -naphthol,  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ ;  $\alpha$ -nitroso- $\beta$ -naphthol methyl ether yielded  $\alpha$ -amido- $\beta$ -naphthol. It is thus clear that these compounds must be naphthaquinoximes,  $\text{C}_{10}\text{H}_6 : \text{NOMe}$ , as if they were true nitroso-compounds,  $\text{MeO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NO}$ , they must have yielded compounds of the formula  $\text{MeO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ , when reduced.

L. T. T.

**Ethylphenol.** By G. ERRERA (*Gazzetta*, 14, 484—486).—In order to prepare ethylphenol by Liebermann's process for the synthesis of phenols (Abstr., 1882, 171) equal molecular proportions of ethyl

alcohol and phenol were heated with zinc chloride, and the product of the reaction, after suitable purification, was fractionally distilled. The greater part passed over between 204—215°, from one portion of which (b. p. 207—211°) was prepared an acetyl-derivative,



boiling at 223—226.1°, and a sulphonic acid, whose barium salt gives Baumann's reaction, common to paraethylphenol and cresol; the other portions were converted into the ethyl ether, boiling at about 200°, and yielding, on oxidation, with permanganic acid, ethylparahydroxybenzoic acid. From these results, it appears that the product of the above reaction consists of isomeric ethylphenol, of which the [1 : 4] derivative predominates. The author considers that the ethylphenol obtained by Auer (Abstr., 1884, 1002) was not a homogeneous substance, and probably was not identical but merely isomeric with the  $\beta$ -ethylphenol obtained by Beilstein and Kuhlberg. V. H. V.

**Cumyl Ether.** By M. FILETI (*Gazzetta*, 14, 496—504).—In the course of the preparation of cumyl alcohol by the action of alcoholic potash on the corresponding aldehyde, a liquid of high boiling point was obtained, the formation of which was ultimately traced to the presence of extraneous inorganic substances, in the course of the purification processes. The liquid in question was *cumyl ether*,  $(\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{CH}_2)_2\text{O}$ , derived from the cumyl alcohol by dehydration. This substance can, however, be more conveniently prepared by the action of sodium cumolate on chlorocymene, or by the distillation of cumyl alcohol with dilute sulphuric acid. Thus prepared cumyl ether is an oily liquid boiling at 350° with partial decomposition into cumaldehyde and cymene, a change which becomes complete at 370°. The product of decomposition was identified by the formation of a crystalline sodium hydrogen sulphite compound from the one, and the formation of cymenesulphonic acid from the other. It is observed that of the two isopropyl-groups originally present in the cumyl ether, the one remains unaltered, while the other is transferred into the normal propyl-group, as shown by the formation of cymene instead of isocymene.

The author considers that the decomposition of an ether into an aldehyde and hydrocarbon thus,  $\text{CH}_2\text{R}\cdot\text{O}\cdot\text{CH}_2\text{R} = \text{R}\cdot\text{CHO} + \text{R}\cdot\text{CH}_3$ , may prove to be of general application; this change has already been observed in the case of benzyl and ethyl ethers by Cannizzaro and Liebig respectively. V. H. V.

**Azoresorcinol and Azoresorufin.** By H. BRUNNER (*Ber.*, 18, 580—591).—A reply to Weselsky and Benedikt (*Monatsh. Chem.*, 5, 605). After a discussion of these investigators' objections to the formulæ put forward by Brunner and Krämer (Abstr., 1884, 1335), and a careful comparison of the two sets of results obtained, the author maintains the correctness of his and Krämer's formulæ.

L. T. T.

**Pipitzahoic Acid.** By R. ANSCHÜTZ (*Ber.*, 18, 709—715).—Pipitzahoic acid was discovered by Weld (*Annalen*, 95, 188), who assigned to it the formula  $\text{C}_{15}\text{H}_{20}\text{O}_3$ . The author confirms this

formula. The acid melts at 102—103°, and can be sublimed; it is insoluble in cold, nearly insoluble in hot water, readily soluble in alcohol, ether, chloroform, carbon bisulphide, and benzene. It distils with steam. When distilled with zinc-dust, a small quantity of a mobile colourless liquid is obtained, but was not further investigated. Pipitzahoic acid appears to be a hydroxyquinone. Its metallic salts are decomposed by carbonic anhydride. It is reduced and dissolved by alcoholic sulphurous anhydride; on exposing the pale yellow solution to air, oxygen is absorbed and pipitzahoic acid again formed. Pipitzahoic acid reacts with aniline to form a compound of the formula  $C_{15}H_{19}O_3 \cdot NHPh$ ; this crystallises in small prismatic violet needles, melts at 133—137°, and sublimes in steel-blue needles. The mother-liquors from this compound contain the reduction-product (quinol) of pipitzahoic acid, which, on exposure to air, absorbs oxygen and precipitates the acid. From these results, it would appear that pipitzahoic acid contains only one benzene-ring, that it is a hydroxyquinone, and that there is as yet no evidence of the nature of the order of combination of the other elements. A. J. G.

**Derivatives of Pipitzahoic Acid.** By R. ANSCHÜTZ and W. LEATHER (*Ber.*, 18, 715—717).—Acetylpipitzahoic acid,  $C_{15}H_{19}O_3 \cdot Ac$ , is prepared by heating the acid with twice its weight of acetic anhydride. It forms large colourless rhombic crystals; axial ratios—

$$a : b : c = 0.62933 : 1 : 0.84507,$$

and melts at 115°.

*Ethyl pipitzahoate* prepared by the action of ethyl bromide on the silver salt, forms small transparent crystals and melts at 141°.

The *paratoluidine-derivative*,  $C_{15}H_{19}O_3 \cdot NH \cdot C_6H_4Me$ , prepared by mixing alcoholic solutions of paratoluidine and the acid, forms bluish-violet needles melting at 132—134°. The orthotoluidine-derivative resembles its isomeride, and melts at 108—110°.

*Hydroxypipitzahoic acid*,  $C_{15}H_{20}O_4$ , is prepared by heating the alcoholic solutions of the aniline or toluidine derivatives after acidifying with sulphuric acid. It crystallises in lustrous reddish-yellow plates, melts at 129°, and dissolves in alkalis to violet-red solutions, from which it is reprecipitated by carbonic anhydride. It does not react with aniline and its homologues.

Pipitzahoic acid unites with bromine, forming a crystalline compound melting at 109—110°. A. J. G.

**Pipitzahoic Acid or Perezone.** By F. MYLIUS (*Ber.*, 18, 936—947; for previous note see this vol., p. 805).—Pipitzahoic acid is not a true acid but a hydroxyquinone, containing the group  $C_6H_{17}$ ; the author suggests the name *perezone*, and expresses the constitution thus:  $C_9H_{17} \cdot C_6H_2O_2(OH)$ . Perezone readily reacts with hydroxylamine, the product crystallising in flat, violet-brown needles, melting at 153—154°; this compound is named *perezonoxime*,



It is insoluble in water, but yields purple-red solutions with ether, alcohol, chloroform, benzene, and with concentrated sulphuric acid,

and a blue-violet solution with alkalis. When it is heated with hydrochloric acid, it does not yield hydroxylamine and perezone as might have been expected, but is converted into ammonia and hydroxyperezone. From this reaction it seems possible that perezone-oxime may not be an oxime, but the amide of an acid,  $C_{15}H_{19}O_3 \cdot NH_2$ , the hydroxyperezone being in fact a sort of acid. Perezone-oxime is very stable; it can be sublimed and may be boiled with aniline without decomposition. When the alcoholic solution is heated with stannous chloride, it becomes azure-blue and finally colourless, the product becoming blue again on oxidation with ferric chloride. Perezone reacts with bases according to the equation



a portion of the perezone becoming reduced to hydroperezone. By the action of methylamine on perezone, a resinous mass is formed, and when this is separated and the solution treated with hydrochloric acid, *methylamidoperezone*,  $C_{15}H_{19}O_3 \cdot NHMe$ , is precipitated. This crystallises from alcohol in blue needles, melting at  $112-114^\circ$ , is insoluble in water, readily soluble in alcohol, ether, and in alkalis, also soluble in sulphuric acid, from which it is reprecipitated on dilution. All the compounds of perezone with primary bases are blue and their solutions purple-red. *Anilidoperezone*,  $C_{15}H_{19}O_3 \cdot NHPh$ , is obtained by heating an alcoholic solution of perezone with aniline. It melts at  $138-139^\circ$ , is insoluble in water, sparingly soluble in alcohol, readily in ether, light petroleum, benzene, glacial acetic acid, chloroform, and carbon bisulphide, dissolves sparingly in alkali, is insoluble in hydrochloric acid; concentrated sulphuric acid dissolves it with deep blue coloration, the solution becoming cherry-red on heating and then yellow. When the alcoholic solution is heated with stannous chloride, it becomes colourless, anilidohydroperezone being produced. Ortho- and para-toluidine react with perezone in the same way as aniline, the products being very similar to that just described. The orthotoluidine-derivative,  $C_{15}H_{19}O_3 \cdot NHC_7H_7$ , melts at  $135-136^\circ$ , and the paratoluidine compound at  $133-135^\circ$ . With metamidobenzoic acid, perezone yields a violet-red compound.

*Hydroxyperezone*,  $C_{16}H_{20}O_4$ , is obtained on boiling a solution of anilidoperezone in glacial acetic acid with dilute sulphuric acid. It forms yellowish-red scales, melting at  $133-134^\circ$ , is almost insoluble in water, readily soluble in alcohol, chloroform, glacial acetic acid, and benzene, more sparingly in light petroleum. When anilidoperezone is decomposed by means of hydrochloric acid, the product retains some of the latter acid even after recrystallisation, and melts only at  $165-168^\circ$ , from which it appears that the hydrochloric acid is held in chemical combination in the unsaturated group  $C_9H_{17}$ . Hydroxyperezone is a feeble acid, is soluble in alkalis, their carbonates, and in ammonia with violet coloration; the salts of the alkalis are very soluble, those of the heavy metals are mostly reddish amorphous precipitates. When the cherry red solution in concentrated sulphuric acid is heated at  $60-80^\circ$ , the colour changes to yellow, and on then diluting with water, *perezinone*,  $C_{15}H_{18}O_3$ , separates. This is moderately soluble in alcohol and ether, more readily in benzene and chloroform; it crystallises in pale

yellow needles or prisms, melting at  $143-144^{\circ}$ . It may be reduced to a colourless phenol by treating its alcoholic solution with zinc and hydrochloric acid. Perezinone possesses feebly acid properties; the sodium ( $C_{15}H_{17}O_3Na$ ), potassium, and ammonium derivatives are very similar; their solutions are readily decomposed by the carbonic anhydride in the air with separation of perezinone. The composition of the sodium salt shows perezinone to be a monobasic phenol, and since it results from the abstraction of  $H_2O$  from hydroxyperezone, the latter must be assumed to contain two hydroxyl-groups. In support of this, perezinone is found to give a garnet-red coloration with Millon's reagent, whilst hydroxyperezone gives a lemon-yellow colour (see Baumann, *Ber.*, **12**, 1452). A. K. M.

**Action of Bromine on Eugenol.** By L. CHASANOWITZ and C. HELL (*Ber.*, **18**, 823-824).—*Dibromeugenol dibromide*,



is obtained by treating eugenol (1 mol.) with an excess of bromine (3 mols.). It crystallises in brilliant quadratic or short rhombic tables, melts at  $118-119^{\circ}$ , and is but slightly soluble in cold ether or alcohol. Zinc-dust acts very energetically on the hot alcoholic solution, *dibromeugenol*,  $HO \cdot C_6HBr_2(OMe) \cdot C_3H_5$ , being formed; this compound is very soluble in alcohol, and by slow evaporation of the cold alcoholic solution, it is obtained in glistening prismatic crystals of the hexagonal system; it melts at  $59^{\circ}$ . When treated with bromine it yields the dibromide. A. P.

**Hexahydroxybenzene-derivatives and their Relation to Croconic and Rhodizonic Acids.** By R. NIETZKI and T. BENCKISER (*Ber.*, **18**, 499-517).—A method of preparing nitranilic acid was described by Nietzki (*Abstr.*, 1884, 58), and the authors now bring forward the following modification: diacetylquinol (1 part) is added to nitric acid of sp. gr. 1.48-1.5 (6 parts), the temperature being maintained at about  $10^{\circ}$ ; the mixture is then cooled to about  $-8^{\circ}$ , and sulphuric acid (6 parts) also at  $-8^{\circ}$  carefully added, taking care that the temperature does not rise above  $0^{\circ}$ ; the product is kept for some hours at  $-3^{\circ}$  to  $0^{\circ}$ , and the crystalline paste then poured on 12-15 parts of crushed ice. The nitranilic acid which separates is collected and converted into the potassium salt. Nitramidotetrahydroxybenzene has been described by Nietzki (*loc. cit.*): its solution in potash becomes black on exposure to the air, from the formation of *dipotassium nitramidodihydroxyquinone*,  $NO_2 \cdot C_6(NH_2)(OK)_2O_2$ ; it crystallises in long black needles of coppery lustre. When its concentrated solution is treated with hydrochloric acid, it becomes yellow, and the monopotassium-derivative,  $NO_2 \cdot C_6(NH_2)(OK)(OH)O_2$ , separates in small orange-red prisms.

When nitramidotetrahydroxybenzene is made into a paste with dilute hydrochloric acid, the mixture well cooled with ice, and a concentrated solution of sodium nitrite gradually added, nitric oxide is abundantly evolved and a clear solution obtained, which deposits



gold-coloured needles of a diazo-compound,  $C_6H_4NaN_3O_8$ . This is moderately soluble in water, but is reprecipitated by the addition of alcohol; its aqueous solution is decomposed by boiling, and when the dried substance is heated, it explodes with great violence.

*Diamidotetrahydroxybenzene* is obtained by warming nitramido-tetrahydroxybenzene with an acid solution of stannous chloride, and an excess of tin; it is also prepared from potassium nitranilate. The hydrochloride,  $C_6(OH)_4(NH_2, HCl)_2$ , forms long colourless needles, very readily soluble in water, but precipitated from the solution by the addition of hydrochloric acid. The separated base at once becomes brown from atmospheric oxidation, whilst oxidising agents produce an almost black crystalline precipitate of *di-imidedihydroxyquinone*,  $C_6(NH)_2(OH)_2O_3$ . If the hydrochloride is boiled with anhydrous sodium acetate and an excess of acetic anhydride, the acetyl-derivative,  $C_6(OAc)_4(NHAc)_2$ , is formed, and crystallises in small colourless plates melting at about  $240^\circ$  with partial decomposition. On boiling this with concentrated hydrochloric acid, the amidoacetyl-groups appear to be eliminated, whilst the base formed is converted by oxidation into a crystalline di-imide.

Attempts to prepare a diazo-derivative from diamidotetrahydroxybenzene yielded the di-imide, and by further action a colourless crystalline substance,  $C_6H_4O_{14}$ , free from nitrogen. This compound is almost insoluble in water, alcohol, and ether, but crystallises from warm dilute nitric acid in microscopic needles; when heated with water, it is decomposed at about  $90^\circ$ , with evolution of gas and formation of a clear yellowish-brown liquid; it melts at about  $95^\circ$ , and gives off water (about 34 per cent.) and carbonic anhydride (about 10 per cent.), the residue dissolving very readily in water to a reddish-brown liquid. When it is acted on by a strongly acid solution of stannous chloride, a substance (*hexahydroxybenzene?*) is obtained crystallising in long needles; this is sparingly soluble in cold, somewhat more readily in hot water, and is precipitated from its solution by the addition of hydrochloric acid; sparingly soluble also in alcohol, ether, and benzene, the solutions rapidly assuming a reddish-violet colour on exposure to the air. Silver nitrate is instantly reduced in the cold; ferric chloride produces a transient violet coloration; concentrated nitric acid converts the substance into the compound  $C_6H_4O_{14}$ ; by the action of phosphorus pentachloride at  $180$ – $200^\circ$ , perchlorethane appears to be produced (comp. Merz and Ruoff, this Journal, 1876, ii, 511). On distilling the substance with zinc-dust, benzene was obtained; a solid substance (? diphenyl) was simultaneously produced. By the action of acetic anhydride and fused sodium acetate on the hexahydroxybenzene, an acetyl-derivative,  $C_6(OAc)_6$ , may be formed; this is almost insoluble in alcohol, ether, and benzene, sparingly soluble in boiling glacial acetic acid, from which it crystallises in small, colourless, well-formed prisms containing acetic acid of crystallisation; it melts at  $203^\circ$ .

When sodium carbonate is added to a saturated solution of hexahydroxybenzene, and a current of air passed into the liquid, the disodium-derivative of *tetrahydroxyquinone*,  $C_6Na_2H_2O_6$ , separates; it forms stellate groups of needles of green metallic lustre. The barium-

derivative,  $C_6BaH_2O_6$ , is also described. If potassium carbonate or hydroxide be employed instead of sodium carbonate, a compound similar in appearance is obtained, but the oxidation appears to be more energetic. Nitric acid converts the sodium and potassium derivatives into the compound  $C_6H_{16}O_{14}$ .

The amount of carbonic anhydride evolved on heating the compound  $C_6H_{16}O_{14}$ , at  $100^\circ$ , corresponds approximately with 1 atom carbon to the molecule  $C_6H_{16}O_{14}$ . The product yields a potassium salt,  $C_6K_2O_6$ , crystallising in long dark yellow needles, and agreeing in composition and properties with Gmelin's *potassium croconate*, the identity being confirmed by direct comparison. The same compound may also be obtained by the action of potash and atmospheric oxygen on tetrahydroxyquinone, or on hexahydroxybenzene, the carbon which is removed being converted into oxalic acid and perhaps partly into carbonic anhydride. The authors refer to the researches of Will (*Annalen*, **118**, 177) and of Lerch (*Annalen*, **124**, 20), some of the compounds described by the latter being apparently identical with those above described, namely hexahydroxybenzene, tetrahydroxyquinone, and the compound  $C_6H_{16}O_{14}$ , which were obtained by Lerch from the compound of potassium with carbonic oxide. When diamidotetrahydroxybenzene hydrochloride is boiled with potash, ammonia is given off, whilst a black crystalline substance separates, and on boiling this with water and evaporating with the addition of some potash, potassium croconate is formed. With regard to the constitution of the compound  $C_6H_{16}O_{14}$  (Lerch's *oxycarboxylic acid*), its relation to hexahydroxybenzene (the formation of one from the other by oxidation and reduction) may be compared to that of a quinone to a hydroquinone, and the authors in fact regard it as a compound of *perquinone*,  $C_6O_6$ , with  $8H_2O$ ;  $C_6O_6 + 8H_2O = C_6H_{16}O_{14}$ . In support of this view it is found that this substance can be reduced by sulphurous acid, and that the sodium-derivative of the reduction product has the composition  $C_6Na_2O_6$ ; by the action of nitric acid on the latter,  $C_6H_{16}O_{14}$  is reproduced. The series,  $C_6(OH)_6$ ,  $C_6O_2(OH)_4$ ,  $C_6O_4(OH)_2$ , and  $C_6O_6$  is thus complete. The name *triquinoyl* is suggested for the last of these, and *dihydroxydiquinoyl* for the compound  $C_6O_4(OH)_2$ . The solution of sodium dihydroxydiquinoyl gives a red precipitate with barium chloride; the silver salt is reddish-violet, crystalline and insoluble. Tetrahydroxyquinone and dihydroxydiquinol are believed to be Lerch's dihydrocarboxylic and carboxylic acids.

A. K. M.

**Action of Nitrous Anhydride on Parabromaniline Nitrate.** By V. OLIVIERI (*Gazzetta*, **14**, 459—460).—In the course of the attempted preparation of parabromophenol from parabromaniline nitrate through the intervention of the diazo-derivative, the nitrous anhydride being furnished from arsenious anhydride and nitric acid, nitrobromophenol was formed. This result was traced to the use of nitric acid of too high sp. gr., and to the production therefrom of nitric peroxide, which effected the nitration of the bromophenol. These results are in accordance with the observations of Stenhouse and Groves and of Lunge, that to obtain pure nitrous anhydride from

nitric acid and arsenious anhydride, concentrated nitric acid must not be used (comp. Trans., 1885, 457). V. H. V.

**Nitroso-derivatives of Aromatic Amines.** By O. N. WITT (Ber., 18, 877—878).—The *nitrosotetramethylphenylenediamine hydrochloride*,  $C_6H_3NO(NMe_2)_2 \cdot HCl$ , is obtained as a dark brownish-red precipitate on adding sodium nitrite to an acid solution of hydrochloride of tetramethylphenylenediamine. It crystallises in dark red lustrous needles; it is soluble in water, forming a deep red solution. The free base is obtained as a deep brown oil on decomposing the hydrochloride with sodium carbonate or hydroxide, and extracting the aqueous solution with ether. This nitroso-compound reacts with amines and phenols, producing colouring matters in a great variety of shades. Tetramethyltoluenediamine appears to form a similar nitroso-derivative. P. P. B.

**Action of Formaldehyde on Aniline.** By L. PRATESI (Gazzetta, 14, 351—356).—Independently of Tollens (Abstr., 1884, 988), the author has examined the action of formaldehyde on aniline, with a view of deciding whether the substances formed are analogous to the diamines isolated by Schiff, that is, homologues of ethylidene, or to the diamines isolated by Hofmann, that is, homologues of ethylene. In this paper it is shown that substances of the latter type are formed, and that as ethylene bromide and aniline form mono- and di-ethylenediphenyldiamine, together with a third base insoluble in alcohol, so formaldehyde and aniline produce mono- and di-methylenediphenyldiamine and a third insoluble base.

By mixing a dilute aqueous solution of oxymethylene with a large excess of aqueous solution of aniline, there is produced *methylenediphenyldiamine*,  $CH_2(NHPh)_2$ , which crystallises in four-sided tables, melting at  $49^\circ$ , soluble in alcohol. It combines with hydrochloric acid, but the product is very unstable. If the aniline is not used in too large an excess, *dimethylenediphenyldiamine*,  $CH_2<\overset{NPh}{\underset{NPh}{|}}CH_2$ , is produced, probably by the decomposition of methylenediphenyldiamine, in accordance with the equation  $2C_{13}H_{14}N_2 = C_{14}H_{14}N_2 + 2C_6H_7N$ . This substance crystallises in prisms, which melt at  $140^\circ$ , and has been described by Tollens under the name of anhydroformaldehydaniline (see above). There is also a third base, probably corresponding with Hofmann's compounds, which is considered to be triethylenetriphenyl-triamine; it is sparingly soluble in alcohol and benzene, and has no definite point of fusion. The analytical results, at present incomplete, seem to indicate a composition expressible by the formula  $C_7H_7N$ , or some multiple of it. It is thus either isomeric or polymeric with dimethylenediphenyldiamine. V. H. V.

**Diphenylamine-derivatives of Succinic Acid.** By A. PIUTTI (Gazzetta, 14, 467—469).—The author has already shown that when diphenylamine is heated with phthalic acid, diphenylamine-phthalein and diphenylphthalamic acid are formed (Abstr., 1884, 451). A

precisely similar reaction occurs between diphenylamine and succinic acid or anhydride. The succinic acid homologue of the phthalein,  $(\text{NPh}_2)_2\text{C} < \text{C}_2\text{H}_4 > \text{CO}$ , crystallises in brilliant needles which melt at  $234^\circ$ , and is less soluble in ordinary reagents than the phthalein. By concentrated potash, it is reconverted into diphenylamine and succinic acid; with nitric acid it yields nitro-derivatives, the potassium salts of which are violet.

*Diphenylsuccinamic acid*,  $\text{COOH} \cdot \text{C}_2\text{H}_4 \cdot \text{CONPh}_2$ , crystallises in large rhombic laminae, which melt at  $119^\circ$ . Its alkaline salts are very soluble; its copper and nickel salts form green precipitates. The ferrous and ferric salts are yellow, and the cobalt red. The silver salt is precipitated from dilute solutions in a crystalline form.

V. H. V.

**Derivatives of Diphenylamine-phthalein.** By A. PIUTTI (*Gazzetta*, 14, 470—472).—The diphenylamine-phthalein described by the author (Abstr., 1884, 451), may be conveniently prepared by the addition of phthalic chloride to a slight excess of the base. From the product of the reaction the unaltered diphenylamine is converted into the hydrochloride, and the mass boiled in alcohol, in which the phthalein is practically insoluble. If diphenylamine-phthalein is heated with 2 mols. of phosphorus pentachloride at a temperature of  $100^\circ$ , there is a considerable evolution of hydrogen chloride; the mass is treated with benzene, and the residue therefrom is decomposed by water with production of two crystalline chlorinated compounds melting at  $228^\circ$  and  $138^\circ$  respectively. The former crystallises in glistening prisms soluble in alcohol and ether. The analysis indicated a composition  $\text{C}_{32}\text{H}_{16}\text{Cl}_2\text{O}_7(\text{NPh}_2)_8$ , derived probably by the decomposition of the tetrachlorinated derivative  $\text{CCl}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CCl}(\text{NPh}_2)_2$  with water, thus:  $4\text{C}_6\text{H}_4\text{Cl}_4(\text{NPh}_2)_2 + 7\text{H}_2\text{O} = \text{C}_{13}\text{H}_{16}\text{Cl}_2\text{O}_7(\text{NPh}_2)_8$ . With nitric acid it forms nitro-derivatives, giving a violet coloration with alcoholic potash. The second substance, melting at  $138^\circ$ , is soluble in alcohol, ether, and benzene, but no analyses were made from want of material.

V. H. V.

**Benzoyl-derivatives of Aromatic Amines.** By O. HESS (*Ber.*, 18, 685—688).—Michler has described a dimethylamidodibenzoylbenzene as obtained by the action of benzoic chloride on dimethylaniline (this Journal, 1877, ii, 334). The author has entirely failed to obtain this substance, and finds that the reaction yields benzoylmethylaniline, methyl chloride, and small quantities of paramethamidobenzophenone.

*Benzoylmethylaniline*,  $\text{NMePhBz}$ , forms colourless crystals, melts at  $63^\circ$ , is not readily volatile in steam, and is insoluble in water but soluble in the other ordinary solvents. It is also readily obtained by mixing together methylaniline and benzoic chloride. When heated at  $150^\circ$  in sealed tubes with zinc chloride or hydrochloric acid, it is decomposed into methylaniline and benzoic acid. When nitrated, it yields a mononitro-derivative,  $\text{C}_{14}\text{H}_{12}\text{NO} \cdot \text{NO}_2$ , crystallising in yellow triclinic prisms, which melt at  $111^\circ$ , and a dinitro-derivative,  $\text{C}_{14}\text{H}_{11}\text{NO}(\text{NO}_2)_2$ , crystallising in yellow needles and melting at  $136^\circ$ .

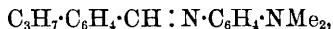
*Benzoylethylaniline*,  $\text{NEtPh}\overline{\text{Bz}}$ , is prepared by heating diethylaniline with benzoic chloride in a reflux apparatus at  $200^\circ$ . It forms large crystals, melts at  $60^\circ$ , boils at  $260^\circ$  under 140 mm. pressure, is readily soluble in ether, alcohol, benzene, &c., but is insoluble in water. When heated with hydrochloric acid, it yields ethylaniline and benzoic acid.

*Benzoylmethyl- $\alpha$ -naphthylamine*,  $\text{NMeBz}\cdot\text{C}_{10}\text{H}_7$ , prepared by heating dimethyl- $\alpha$ -naphthylamine and benzoic chloride in a reflux apparatus at  $170$ — $190^\circ$ , forms colourless crystals, melts at  $121^\circ$ , and is readily soluble in ether, acetone, carbon bisulphide, and hot alcohol, sparingly soluble in cold alcohol.

*Benzoylmethyl- $\beta$ -naphthylamine*,  $\text{C}_{18}\text{H}_{15}\text{NO}$ , prepared in a similar manner to the  $\alpha$ -derivative, crystallises in lustrous, yellow plates, melts at  $169^\circ$ , and is more sparingly soluble in the above solvents than its isomeride.

A. J. G.

**Action of Paramidodimethylaniline on Aldehydes.** By G. NUTH (*Ber.*, 18, 573—575).—This is a continuation of A. Calm's work (this vol., p. 387). Salicylaldehyde gives with paramidodimethylaniline white crystals of *ortho*-hydroxybenzylideneamido-dimethylaniline,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , which melts at  $134^\circ$ , and is easily soluble in alcohol and ether. Under similar conditions cuminaldehyde yields *cumylideneamido-dimethylaniline*,



forming lustrous crystals easily soluble in alcohol and ether, and melting at  $99^\circ$ . Anisaldehyde yields *paramethoxybenzylideneamido-dimethylaniline*, which forms yellow crystals melting at  $139^\circ$ . Parahydroxybenzaldehyde gives *parahydroxybenzylideneamido-dimethylaniline*, crystallising in glistening yellowish scales which decompose at  $240^\circ$ . Cinnamaldehyde forms yellow needles of *phenylallylideneamido-dimethylaniline*,  $\text{CHPh}:\text{CH}\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , which melt at  $141^\circ$ , and are sparingly soluble in cold ether, more readily so in alcohol. Piperonal yields *piperonylideneamido-dimethylaniline*,



a white crystalline powder melting at  $110^\circ$ .

L. T. T.

**Cyanogen Compounds of the Aromatic Diamines.** By J. A. BLADIN (*Ber.*, 18, 666—674).—When cyanogen is passed into an alcoholic solution of [3:4] toluylenediamine, it is absorbed with evolution of heat, whilst the liquid is coloured dark brown; after some days a crystalline mass separates, from which by recrystallisation, treatment with animal charcoal, &c., an additive compound of the formula  $\text{C}_9\text{H}_{10}\text{N}_4 = \text{C}_6\text{H}_3\text{Me} < \begin{smallmatrix} \text{NH}\cdot\text{C}(\text{NH}) \\ \text{NH}\cdot\text{C}(\text{NH}) \end{smallmatrix} >$  is obtained. It crystallises with 1 mol.  $\text{H}_2\text{O}$  in pale-yellow forms, melts at  $242$ — $244^\circ$  with decomposition, but can be partially sublimed, and is readily soluble in alcohol and ether, sparingly soluble in water. It is a strong base,

and forms two series of salts with 1 or 2 mols. of monobasic acids, the latter of which are decomposed by water into the monacid salts. The pure salts are best prepared by precipitating a concentrated alcoholic solution of the base with the respective acids. *Hydrochlorides*:  $C_9H_{10}N_4 \cdot 2HCl$  forms small colourless needles, which lose 1 mol.  $HCl$  when heated at  $160^\circ$ ;  $C_9H_{10}N_4 \cdot 2HCl + 1\frac{1}{2}H_2O$  crystallises in groups of needles. *Platinochlorides*:  $C_9H_{10}N_4 \cdot H_2PtCl_6 + 2H_2O$  forms minute yellow rhombic tables;  $(C_9H_{10}N_4)_2 \cdot H_2PtCl_6 + 2H_2O$  crystallises in yellow needles. The sulphate  $C_9H_{10}N_4 \cdot H_2SO_4 + H_2O$  forms minute tables.

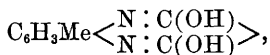
When the cyanogen compound is heated with hydrochloric acid on the water-bath, a new substance,  $C_9H_8N_3O$ , probably



is formed. This crystallises in flat needles, does not melt at  $290^\circ$ , can be sublimed without decomposition, and is sparingly soluble in alcohol and water. It is a feeble base, forming unstable salts with 1 mol. of monobasic acids. It is also soluble in aqueous potash, but is reprecipitated from the solution by carbonic anhydride.

When the compound  $C_9H_{10}N_4$  is heated with water in sealed tubes at  $150^\circ$  for some time, it yields two new substances of the formulæ  $C_9H_8N_2O_2$  and  $C_9H_8N_3O$ . The latter compound is isomeric with that last described; it crystallises in microscopic needles, commences to decompose at  $240^\circ$ , and blackens at  $290^\circ$ , but can be sublimed by careful heating. It is sparingly soluble in alcohol and water, but more soluble than its isomeride. It exhibits feebly acid and basic properties.

The substance  $C_9H_8N_2O_2$  is obtained from the compound  $C_9H_{10}N_4$  or from either of the isomeric compounds  $C_9H_{10}N_3O$  by heating with hydrochloric acid at  $150^\circ$ . It crystallises in long colourless silky needles, does not melt at  $295^\circ$ , and is sparingly soluble in water, more soluble in alcohol. It is an acid, but its salts are unstable. It seems to be identical with the *dihydroxytoluquinoxaline*,



obtained by Hinsberg (Abstr., 1883, 323, 1129; 1884, 1052).

By the action of cyanogen on orthophenylenediamine, the compound  $C_6H_4 < \begin{matrix} NH \cdot C(NH) \\ NH \cdot C(NH) \end{matrix} >$  is obtained. It crystallises in rhombic tables, and can be sublimed, but does not melt at  $280^\circ$ . It closely resembles its homologue. The *platinochlorides*,  $C_8H_8N_4 \cdot H_2PtCl_6 + 3H_2O$ , crystallising in lustrous yellow plates, and  $(C_8H_8N_4)_2 \cdot H_2PtCl_6 + H_2O$ , forming small yellow needles, were obtained.

By the action of hydrochloric acid on the base at  $100^\circ$ , a compound of the formula  $C_6H_4 < \begin{matrix} NH \cdot C(NH) \\ N = C(OH) \end{matrix} >$  is formed; it can be sublimed, does not melt at  $280^\circ$ , is very soluble in water and alcohol, and has both acid and basic properties.

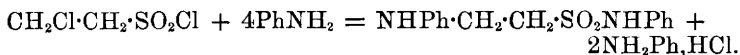
*Dihydroxyquinoxaline*,  $C_6H_4<\begin{smallmatrix} N:C(OH) \\ N:C(OH) \end{smallmatrix}>$ , is formed by heating either of the preceding compounds with hydrochloric acid in sealed tubes at  $150^\circ$ . It crystallises in long colourless needles, does not melt at  $290^\circ$ , and behaves as an acid. A. J. G.

**Mixed Observations.** By H. ECKENROTH (*Ber.*, **18**, 516—518).—*I. Action of Aniline, Ortho- and Para-toluidine, and of Naphthylamine on Diphenyl Carbonate.*—When aniline and diphenyl carbonate are heated together for several hours at  $150$ — $180^\circ$ , magnificent crystals of *carbanilide*,  $CO(NHPh)_2$ , are produced, which are quite colourless after crystallisation from alcohol. *Ortho-* and *para-ditolylicarbamide* and *dinaphthylcarbamide* may be formed in the same way.

*II. Action of Diphenylcarbamide on Diphenyl Carbonate.*—When these substances are heated together, a violent reaction sets in, whilst a strongly refracting liquid distils over, having the odour of phenyl cyanate; this solidifies, however, in a few days to a mass of crystals of phenyl phenylcarbamate,  $NHPh.COOPh$ , melting at  $122^\circ$  (uncorr.) A similar result is obtained with *paraditolylicarbamide*, but the distillate takes longer to solidify, whilst the distillate from *ortho-derivative* remains liquid, and yields only a small quantity of crystals; the distillate from *paraditolythiocarbamide*, on the other hand, separates at once into a liquid and a solid substance.

*III. Action of Carbonyl Chloride on Aldehyde.*—The gas is passed into cooled aldehyde and the product repeatedly distilled, when ethylidene chloride is obtained boiling constantly at  $60^\circ$ . *Paraldehyde* behaves in the same way. A. K. M.

**Action of  $\beta$ -Chlorethylenesulphonic Chloride on Aniline.** By H. LEYMANN (*Ber.*, **18**, 869—872).—When an ethereal solution of aniline is treated with  $\beta$ -chloroethylenesulphonic chloride, the *hydrochloride of phenyltaurine-anilide*, *anhydrophenyltaurine*, *phenyltaurine-anilide*, and *aniline hydrochloride* are formed. The first of these compounds is separated from the mixture by extracting the ethereal solution with dilute hydrochloric acid; it crystallises from alcohol containing hydrochloric acid in crystals, melting at  $169^\circ$ , and when decomposed by alkalis yields the base as an oil, which solidifies after some time, and melts at  $74^\circ$ . The formation of this compound is represented as follows:—



When heated with hydrochloric acid in sealed tubes, the hydrochloride of phenyltaurine anilide is resolved into aniline hydrochloride and phenyltaurine, which is identical with that described by Andreasch (*Abstr.*, 1883, 665), and which the author has prepared by heating an ethereal solution of aniline chlorisethionate with aniline in sealed tubes at  $130^\circ$ .

*Anhydrophenyltaurine*,  $CH_2<\begin{smallmatrix} CH_2 \\ SO_2 \end{smallmatrix}>C_6H_5N$ , is obtained by dissolving in benzene the residue left after evaporating the above-mentioned

etheral solution; the benzene solution on evaporation yields a residue partly crystalline and part liquid. The solid portion when repeatedly crystallised from alcohol, yields *anhydrophenyltaurine* in large white crystals melting at 69°. It is not attacked by caustic alkalis, and when heated in sealed tubes with hydrochloric acid, yields phenyltaurine and other products.

The liquid from which the anhydrophenyltaurine has been separated consists of the *anilide of chloroisethionic acid*,



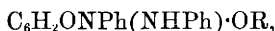
it decomposes on distillation, and is converted by alcoholic potash into anhydrophenyltaurine; when heated with aniline, it forms the hydrochloride of phenyltaurine anilide.

$\beta$ -Chloroethylenesulphonic chloride reacts in a similar manner with toluidine and phenyldiamine, but not with dimethylaniline.

P. P. B.

**Action of the Amines on Quinones.** By T. ZINCKE (*Ber.*, 18, 785—789). — *Dianilido-quinoneanilide*,  $\text{C}_6\text{H}_2\text{ONPh}(\text{NHPh})_2$ , is prepared by treating 1 part of quinone dissolved in glacial acetic acid with 2 parts of aniline; it crystallises in reddish-brown needles, melts at 202—203°, and dissolves in concentrated sulphuric acid with a blood-red colour; it is a feeble base; the hydriodide forms a matted greyish mass; the hydrobromide and hydrochloride are very soluble; the platinochloride cannot be obtained.

The ethers of anilido-hydroxyquinoneanilide,



are obtained by heating the base with sulphuric acid and the respective alcohols. The methyl ether crystallises in large brownish-red tablets, and melts at 188—189°; its salts are mostly of a blue colour, very soluble, and difficult to crystallise. It forms a compound with trinitrophenol, obtained in brownish-violet crystals, melting at 188°; the platinochloride is very soluble, and forms dark shining crystals. The ethyl ether crystallises in red tablets or prisms, and melts at 134°. The isobutyl ether forms fine red needles, and melts at 138°; from this compound *anilido-hydroxyquinoneanilide*,  $\text{C}_6\text{H}_2\text{ONPh}(\text{NHPh})\cdot\text{OH}$ , is obtained by treatment with very dilute alcoholic potash; it forms small scales, having a metallic lustre, and on heating is decomposed without melting; it is sparingly soluble in alcohol, but readily in acetic acid; its metallic derivatives are very soluble; the potassium and sodium compounds have been prepared as silky brown-coloured needles.

If the anilido-oxyquinoneanilide be warmed with a very dilute solution of potash, until the dark-red solution becomes clearer, the addition of acids will precipitate blue crystals of *anilido-hydroxyquinone*,  $\text{HO}\cdot\text{C}_6\text{H}_2\text{O}_2\cdot\text{NHPh}$ ; it is not very soluble in cold, but more so in hot alcohol, and also in glacial acetic acid; concentrated sulphuric acid dissolves it with a brown colour; it decomposes at about 200° without melting; the potassium and sodium-derivatives are very soluble; the silver-derivative forms a dirty reddish-brown precipitate.

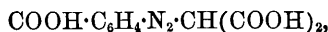
On treating dianilido-quinoneanilide with alcoholic potash at 100°,



a compound is obtained which crystallises in lustrous red needles melting at 191—192°; it is easily soluble in alcohol and benzene; sulphuric acid dissolves it with green coloration, and the addition of water reprecipitates the unaltered compound; it forms salts with bases. Toluquinone yields a similar compound. A. P.

**Diazo-compounds.** By P. GRIESS (*Ber.*, 18, 960—966).—*Chloro-, bromo-, and fluor-benzoic Acids.*—These acids are best prepared by boiling diazobenzoic acid sulphate,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{SO}_4\cdot\text{H}$  (1 part) with the respective halogen acids (3—5 parts). Other haloid substituted aromatic acids, such as metafluorhippuric and orthofluoreinnamic acids, may be obtained in the same way. Orthofluoreinnamic acid,  $\text{C}_6\text{H}_4\text{F}\cdot\text{CH}:\text{CH}\cdot\text{COOH}$ , forms long, white, lustrous needles, very sparingly soluble in hot water, readily in cold alcohol. Previous observations of the author show that hydriodic acid reacts in the same way as the other halogen acids (*Ber.*, 1, 190).

*Azonitromethanebenzoic acid*,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{CH}_2\cdot\text{NO}_2$ .—The preparation of this compound was attempted by Wald (*Ber.*, 9, 393), but with no satisfactory result. The author obtains it thus: an aqueous solution of pure metadiazobenzoic acid nitrate is mixed with a dilute solution of nitromethane in an excess of potash, and in a short time hydrochloric acid is added, when pure azonitromethanebenzoic acid is thrown down as a yellowish-red precipitate. It is moderately soluble in boiling alcohol and ether, very sparingly in boiling water; is almost tasteless, and detonates when heated. Its ammoniacal solution gives a deep red-coloured precipitate with silver nitrate, and no precipitate with barium chloride. *Azoacetoaceticbenzoic acid*,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{CHAc}\cdot\text{COOH}$ , is obtained by the action of metadiazobenzoic acid sulphate on ethyl acetoacetate. It is almost insoluble in boiling water, readily soluble in hot alcohol, from which it crystallises in small scales or needles, which have a bitter taste; when cautiously heated it melts, and at a higher temperature detonates, leaving a carbonaceous residue; the silver salt forms a bright yellow, amorphous precipitate. *Azomalonicbenzoic acid*,



obtained from metadiazobenzoic acid nitrate and ethyl malonate is readily soluble in hot alcohol, and crystallises in microscopic scales or needles.

When metaphenyleneoxamic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_2\text{O}_2\cdot\text{OH}$  (this Journal, 1875, 269), is treated with potassium nitrite in the presence of an excess of hydrochloric acid, the diazo-compound



is produced. On treating the perbromide from this with ammonia,

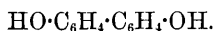
the acid  $\text{N} \begin{array}{c} \diagup \\ \parallel \\ \diagdown \end{array} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{O}_2 \cdot \text{OH}$  is obtained, crystallising in nearly

white needles. When this new acid is boiled with concentrated potash

it yields *metamidodiazobenzimide*,  $\begin{array}{c} \text{N} \\ \parallel \\ \text{N} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , and oxalic acid.

Amidodiazobenzimide is a yellowish oil, having an odour of benzaldehyde; it is volatile in steam, dissolves readily in alcohol and ether, and yields crystalline salts; the hydrochloride,  $\text{C}_6\text{H}_5\text{N}_4\text{HCl}$ , and platinochloride are described. By the action of nitrous acid on a solution of the base in hydrochloric acid, a diazo-derivative ( $\text{N}_3\text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl}$ ?) is obtained which yields coloured azo-compounds with phenols and amines. By the action of stannous chloride on the compound  $\text{ClN}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{O}_2 \cdot \text{OH}$ , a substance,  $\text{NH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{O}_2 \cdot \text{OH}$ , is formed, crystallising in small, white grains, almost insoluble in boiling water, alcohol, and ether. When this is boiled with concentrated hydrochloric acid it gradually dissolves, with formation of oxalic acid and *amidophenylhydrazine*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH}_2$ ; this forms a brownish-coloured, varnish-like mass, which is almost without odour, but has a strong bitter taste. It is readily soluble in alcohol and ether, and very sparingly in water; is very sensitive to oxidising agents, being at once decomposed by Fehling's solution. Its hydrochloride is described.

When a concentrated aqueous solution of diazobenzene hydrochloride is mixed with an equal volume of strong hydrochloric acid, and then with a solution of stannic chloride, *diazobenzene stannochloride*,  $(\text{PhN}_2\text{Cl})_2\text{SnCl}_4$ , separates in white scales, very sparingly soluble in alcohol and ether; it decomposes when heated with production of chlorobenzene; and when boiled with water it yields phenol, nitrogen being evolved. By long exposure to the air it undergoes change, the greater part being apparently converted into paradiphenol,



A. K. M.

### Reduction of Nitrazo-compounds and Azonitrolic Acids.

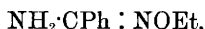
By J. V. JANOVSKY (*Monatsh. Chem.*, **6**, 157—167).—*Dinitroazobenzene* melting at  $206^\circ$ , was prepared by direct nitration of azobenzene, and is probably identical with a substance prepared by Gerhardt; its constitution is  $[\text{NO}_2 : \text{N}_2 : \text{NO}_2 = 4 : 1 : 4]$ . By the action of ammonium sulphide in alcoholic solution, it becomes olive-green and then dark brown; addition of acid produces in each case a precipitate.

The first product is yellow, crystallises well from acetone, and melts at  $218^\circ$ . It has feebly acid properties, dissolving in alkalis with a deep blue colour; its composition is  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NOH}$ , and it is therefore a nitrolic acid. The second product of the reduction is probably  $\text{C}_{12}\text{H}_8\text{N}_2(\text{NOH})_2$ ; it forms dark red crystals. By still further reduction basic substances, probably diamidoazobenzene, &c., are formed.

*Mononitroazobenzene* melting at  $137^\circ$ , was also prepared by direct nitration. Heated with ammonium sulphide in alcoholic solution, the solution becomes first violet, and gives with acids a yellowish precipitate which, like the two preceding substances, dissolves with a deep blue colour in alkalis; it is therefore a nitrolic acid, and its reduction to paraphenylenediamine and aniline show it to have the formula  $\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NOH}$   $[\text{N}_2 : \text{NOH} = 1 : 4]$ ; it melts at  $134^\circ$ .

During the nitration of azobenzene, other nitro-products are obtained if the temperature is high. Their examination is still incomplete. H. B.

**Relations of Benzenylamidoxime-derivatives to the Benzhydroxamic Group.** By F. TIEMANN and P. KRÜGER (*Ber.*, 18, 727—752).—A continuation of the authors' work on the amidoximes (*Abstr.*, 1884, 1325). *Benzenylamidoxime ethyl ether*,



is prepared by the action of sodium ethoxide and ethyl ether on an alcoholic solution of benzenylamidoxime. It crystallises in lustrous, white, rhombic plates, melts at 67°, and is nearly insoluble in water, readily soluble in alcohol, ether, benzene, and chloroform. It is insoluble in alkalis, readily soluble in acids; the hydrochloride crystallises well.

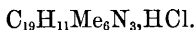
*Benzenylethoxime chloride*,  $\text{CPhCl} : \text{NOEt}$ . By the action of sodium nitrite on benzenylamidoxime ethyl ether hydrochloride, there was obtained, not as was expected, a hydroxy-compound of the formula  $\text{HO}\cdot\text{CPh} : \text{NOEt}$ , but the corresponding chloride. This is an oil boiling at 230° under the atmospheric pressure, and at 125° under a pressure of 45 mm.; it does not solidify at  $-10^\circ$ . It is nearly insoluble in water, readily soluble in alcohol, ether, chloroform, benzene, and light petroleum. It is distinguished from all other imido-chlorides of analogous constitution by its stability towards water, alcohol, acids, and bases. By heating with alcoholic ammonia at 160—180°, it is reconverted into benzenylamidoxime ethyl ether.

*Ethyl benzhydroximate*,  $\text{HO}\cdot\text{CPh} : \text{NOEt}$ , is obtained, but only in an impure state, by the action of sodium nitrite on the sulphate of benzenylamidoxime ethyl ether, the liquid being continuously shaken with ether during the reaction, to remove the product as fast as it is formed. It forms an oil, rapidly decomposed by water into benzoic acid and ethylhydroxylamine. Alkalis partly convert it into a condensation-product.

*Benzenylethoximido-ethyl ether*,  $\text{EtO}\cdot\text{CPh} : \text{NOEt}$ . By the action of alcoholic potash on benzenylethoxime chloride, benzoic acid and ethylhydroxylamine are formed; if, however, the chloride is dissolved in absolute alcohol and treated with sodium ethoxide, benzenylethoximido-ethyl ether is obtained. It is an oil boiling at 238° (uncorr.) under atmospheric pressure, and at 128° under 40 mm. pressure. It is insoluble in water, readily soluble in alcohol and ether. Its alcoholic solution, when heated, is decomposed into ethyl benzoate and ethylhydroxylamine. Alcoholic ammonia at 160—180° converts it into benzenylamidoxime ethyl ether. It is identical with Lossen and Zanni's ethylic  $\alpha$ -ethylbenzhydroxamate (*this Journal*, 1877, 183).

The greater part of the paper is devoted to the consideration of the constitutions of these and allied substances. A. J. G.

**Crystallised Methyl-violet.** By A. W. HOFMANN (*Ber.*, **18**, 767—771).—This substance occurs in commerce. It can be prepared by treating dimethylaniline with a chlorinated methyl formate in presence of aluminium chloride, and seems to be identical with one of the products of the action of carbonyl chloride on dimethylaniline. It crystallises in hexagonal forms, axial ratio  $a : c = 1 : 0.4915$ ; observed faces, P,  $\infty$ P; the crystals are opaque and have a peculiar brownish-green metallic lustre. It dissolves in water and alcohol with deep violet-blue colour. The analytical results show that it most probably is *hexamethylpararosanine hydrochloride*,



The platinochloride,  $(\text{C}_{19}\text{H}_{12}\text{Me}_6\text{N}_3\text{Cl})_3\cdot 3\text{PtCl}_4$ , is obtained as a crimson-red crystalline precipitate. When treated with aqueous ammonium sulphide, the hydrochloride yields a *leuco-base*,  $\text{C}_{19}\text{H}_{13}\text{Me}_6\text{N}_3$ , crystallising in long needles and melting at  $173^\circ$ . This melting point agrees with that of the leuco-base obtained by O. Fischer from the hexamethylrosaniline salt.

A. J. G.

**Preparation of Metanitrocinnamaldehyde.** By F. KINKELIN (*Ber.*, **18**, 483—485).—Attempts to prepare this compound by heating metanitrobenzaldehyde with acetaldehyde, water, and soda, in the proportions given by Piene for the preparation of cinnamaldehyde (*Abstr.*, 1884, 1345), resulted in the production of only a small yield of metanitrocinnamaldehyde, and still poorer results were obtained by Baeyer and Drewsen's method (*Abstr.*, 1884, 58). A yield equal to 50 per cent. of that required by theory, may, however, be obtained as follows:—100 grams of metanitrobenzaldehyde are dissolved in 2 litres of alcohol, 4 litres of water added, and the turbid liquid at once mixed with 35 grams commercial acetaldehyde and 70 grams of a 10 per cent. soda solution. The reaction commences at once, and is complete in 12 hours. The nitrocinnamaldehyde is freed from adhering oil, washed with water, dried at  $30\text{--}40^\circ$ , and finally washed with a little ether and crystallised from hot aqueous alcohol. It melts at  $116^\circ$ , is sparingly soluble in hot water, in cold alcohol, and in ether, readily in benzene and glacial acetic acid; it crystallises from hot water in long slender needles and from alcohol in long thin prisms. The *phenylhydrazine-derivative*,  $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2$ , forms garnet-red plates melting at  $160^\circ$ ; the *anilide* is an oil, the hydrochloride of which forms yellow needles. Metanitrocinnamaldehyde combines with 2 mols. bromine to form an unstable oily additive compound, and on warming this with a solution of sodium acetate, hydrogen bromide is eliminated, and a crystalline compound,  $\text{C}_9\text{H}_5\text{BrNO}_3$ , is produced; this forms long slender needles melting at about  $90^\circ$ . The phenylhydrazine-derivative,  $\text{C}_{15}\text{H}_{12}\text{N}_3\text{BrO}_2$ , crystallises in lustrous golden-yellow scales, melting at  $120^\circ$ .

A. K. M.

**Action of Aldehyde on Metanitrobenzaldehyde.** By C. F. GÖHRING (*Ber.*, **18**, 719—721).—The author dissents from Kinkelin's statement (preceding Abstract) that a very bad yield of metanitro-

cinnamic acid is obtained by the action of aldehyde on metanitrobenzaldehyde, according to Baeyer and Drewsen's method (comp. Abstr., 1884, 58), and states that in his hands the method gives nearly quantitative results.

*Metanitrophenyllactic aldehyde*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COH}$ , obtained as an intermediate product, crystallises in concentrically grouped, colourless needles, decomposed on heating at  $100^\circ$ , readily soluble in ether, sparingly in alcohol, insoluble in water. When boiled with water it is converted into metanitrocinnamaldehyde; the author's description of this latter substance agrees with that given by Kinkelin.

A. J. G.

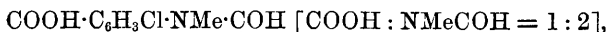
**Occurrence of Benzoic Acid in Coal-tar Oils.** By K. E. SCHULZE (*Ber.*, 18, 615—617).—The author has isolated benzoic acid from the high fractions obtained in the separation of the higher phenols from coal-tar.

L. T. T.

**Conversion of Ethyl Carbanilate into Amidobenzoic Acid.** By W. HENTSCHEL (*Ber.*, 18, 977—981).—The author has shown that the action of sulphuric acid on carbanilide yields sulphanilic and amidosulphobenzoic acids (Abstr., 1884, 1016). The temperature required for this reaction is about  $100^\circ$ ; if it be raised a little above this, carbonic anhydride is evolved, and sulphanilic acid alone obtained. Owing to the difficulty of separating the amidosulphobenzoic from the sulphanilic acid, experiments were made with the view of obtaining the former acid by itself. Phenylcarbamide dissolves in fuming sulphuric acid with considerable evolution of heat, but the product contains both the above acids. The action of sulphuric acid on methyl carbanilate yields, however, the desired result. The carbanilate is best obtained by agitating aniline and methyl chloroformate with water; it is dissolved in fuming sulphuric acid, the product poured into water and converted into lead salt. *Methylamidosulphobenzoate*,  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{COOMe})\cdot\text{SO}_3\text{H}$ , forms prismatic crystals, readily soluble in water and alcohol; it melts at  $188^\circ$  with evolution of carbonic anhydride and formation of sulphanilic acid. Sulphuric and hydrochloric acids at  $150^\circ$  also decompose it with formation of the same products.

A. K. M.

**Methylformylorthamidochlorobenzoic Acid and Methylpseudochlorisatin from Metachloroquinoline Methyl Chloride.** By W. LA COSTE and J. BODEWIG (*Ber.*, 18, 428—432).—With the view of ascertaining the position of the chlorine-atom in the metachloroquinoline obtained from metachloraniline (Abstr., 1884, 1196), the authors have oxidised metachloroquinoline methyl chloride by means of potassium permanganate (compare Claus and Glyckherr, Abstr., 1883, 1009), but the experiments are not yet complete. The oxidation-product is filtered, acidified with hydrochloric acid, and allowed to remain for 12 hours. The crystalline precipitate contains *methylformylorthamidochlorobenzoic acid*,



and *methylpseudochlorisatin*,  $\text{C}_6\text{H}_3\text{Cl} < \begin{smallmatrix} \text{CO} \\ \text{NMe} \end{smallmatrix} > \text{CO}$ . The first-named compound crystallises in scales or needles, melts at  $201\text{--}202^\circ$  with decomposition, dissolves readily in hot alcohol, in alkalis, and alkaline carbonates, sparingly in ether and chloroform, and only to a slight extent in boiling water. When boiled with a little dilute hydrochloric acid, it yields formic and *methylamidochlorobenzoic acids*, whilst concentrated hydrochloric acid converts it into carbonic anhydride and metachloromonomethylaniline, the hydrochloride of which forms large, transparent, four-sided plates or stellar groups of needles, melting at  $164^\circ$ ; the free base is a colourless oil boiling at about  $240^\circ$ .

*Methylorthamidochlorobenzoic acid*,  $\text{NHMe}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{COOH}$ , is most readily obtained by heating the formyl-derivative with alcoholic potash; it is very sparingly soluble in water, readily in alcohol, and crystallises in slender, white needles melting at  $178^\circ$ ; the alkali salts dissolve readily in water and alcohol.

*Methylpseudochlorisatin* is sparingly soluble in cold, somewhat more readily in boiling water, in alcohol and ether, and very readily in chloroform. It crystallises in long, red, silky needles, resembling alizarin, melts at  $191^\circ$ , and may be sublimed without decomposition. It yields the indophenine reaction with coal-tar benzene and sulphuric acid. It is almost insoluble in cold solutions of alkaline carbonates, sparingly soluble in dilute ammonia, readily in caustic alkalis with bright yellow coloration; it possesses only feebly acid properties, carbonic anhydride precipitating it from its solution in baryta-water.

A. K. M.

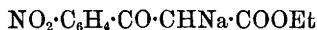
**Action of Phenylbromacetic Acid on Ethyl Acetate and Derivatives of Phenylacetosuccinic Acid.** By A. WELTNER (*Ber.*, 18, 790—795; comp. Abstr., 1884, 746).—The second possible phenylacetosuccinic acid is prepared by treating sodium phenylbromacetate suspended in alcohol with an equivalent quantity of ethylic sodacetate; it forms lustrous scales, melts at  $128^\circ$ , and is easily soluble in alcohol. Unlike its isomeride, it is a stable compound, and forms stable salts. The *silver salt*,  $\text{C}_{14}\text{H}_5\text{O}_5\text{Ag}$ , forms granular crystals; it may be heated at  $200^\circ$  without any evolution of carbonic anhydride; on heating it with barium hydroxide phenyllævulinic acid is formed. By the action of sodium amalgam, it is converted into *phenylvalerolacetocarboxylic acid*,  $\text{O} < \begin{smallmatrix} \text{CO}\cdot\text{CHPh} \\ \text{CHMe}\cdot\text{CH} \end{smallmatrix} > \text{CH}\cdot\text{COOH}$ , which crystallises in quadratic scales, and melts at  $167\cdot5^\circ$ . The *barium* and *silver salts* are readily soluble in water. The *calcium salt* was also prepared. By heating the acid with barium or calcium hydroxide, it is converted into the *bibasic acid*,  $\text{HO}\cdot\text{CHMe}\cdot\text{CH}(\text{COOH})\cdot\text{CHPh}\cdot\text{COOH}$ ; salts of this acid are only stable in alkaline solutions, as on heating the solution of the pure salts, they are decomposed with formation of a monobasic lactonic acid.

Phenylhydrazine compounds may be prepared both from ethylic phenylacetosuccinate and from phenyllævulinic acid. Thus on heating the alcoholic solution of phenylacetosuccinic acid with phenylhydrazine acetate, the compound,  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4$ , is precipitated in thin scales which may be recrystallised from alcohol; it melts at  $149^\circ$ . The

*phenyllævulinic acid hydrazine compound*,  $C_{17}H_{18}N_2O_4$ , is obtained in a similar way in matted needles; it melts at  $140^\circ$ : both these hydrazine compounds are acted on by light, turning a dark brown colour, and becoming semi-fluid. By the action of alcoholic ammonia on phenylacetosuccinic acid in a sealed tube, two compounds are formed; one crystallises in brilliant prisms which melt between  $260^\circ$  and  $270^\circ$ , and has the composition  $C_{12}H_{12}N_2O_2$ ; it dissolves slowly in dilute soda, with evolution of ammonia, and an acid,  $C_{12}H_{11}NO_3$ , crystallising in needles, and melting at  $148-149^\circ$ , is produced. The other acid, formed by the action of ammonia on phenylacetosuccinic acid, crystallises in long, silky needles; it melts at  $128-129^\circ$ , and is soluble in concentrated hydrochloric acid; if heated with barium hydroxide, it gives off carbonic anhydride and ammonia, and yields phenyllævulinic acid; its composition is probably  $C_{13}H_{15}NO_3$ . A. P.

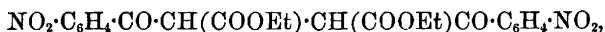
**Action of Light on Nitrocumic Acid.** By P. ALEXÉEFF (*J. Russ. Chem. Soc.*, 1885 [1], 112—114).—Paternò and Fileti (Abstr., 1876, i, 595) found nitrocumic acid to be converted by light into a bright red substance insoluble in benzene, but soluble in alkaline solutions. The author states that by reducing the red compound with zinc-dust and potash, or with sodium amalgam, a colourless solution is obtained, which, on treatment with acids, yields a white amorphous precipitate, rapidly becoming red in contact with air, and then exhibiting a close resemblance to the original red compound. Hence nitrocumic acid gives under the influence of light a true colouring matter. Presuming that the process under consideration might be analogous to the action of sulphuric acid on some nitro-compounds, and consist in an oxidation of the tertiary hydrogen of the isopropyl at the expense of the nitro-group, and subsequent condensation of the nitro-product formed (Abstr., 1884—Lifschutz, 1187, and Brunner Krämer, 1354), the author intends studying the behaviour of different nitro-compounds towards light. Thus far he has been able to observe that light acts in much the same manner as on nitrocumic acid, on its aldehyde, nitrocumol, and its ethyl ether, the latter yielding a compound apparently identical with that formed by passing hydrogen chloride through an alcoholic solution of the red product from nitrocumic acid. Nitrohydroxycumic acid, containing hydroxyl in the place of the tertiary hydrogen of nitrocumic acid, is not acted on by light. A. T.

**Paranitrobenzoylacetic Acid.** II. By W. H. PERKIN, Jun., and G. BELLENOT (*Ber.*, 18, 951—960; comp. Abstr., 1884, 1023). When sodium ethylate is added to ethyl paranitrobenzoylacetate dissolved in a little absolute alcohol, the sodium-derivative



is produced. It is very stable, behaves like the salt of an acid, and can be crystallised from water. When treated with ethyl iodide, it yields *ethylic ethylparanitrobenzoylacetate*,  $NO_2 \cdot C_6H_4 \cdot CO \cdot CHEt \cdot COOEt$ , which forms colourless nacreous scales, melting at  $39-40^\circ$ . All

attempts to prepare ethylparanitrobenzoylacetie acid failed. *Ethylie diparanitrobenzoylsuccinate*,



is prepared by gradually adding iodine, dissolved in pure ether, to finely powdered ethyl paranitrobenzoylsodacetate, and vigorously agitating; the excess of iodine is removed by the addition of a few drops of sulphurous acid, the sodium iodide filtered off, and the ether evaporated; the product crystallises from dilute alcohol in colourless crystals, melting at  $180^\circ$ . When its solution in dry ether is treated with an ethereal solution of sodium ethylate, a white amorphous powder (probably  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CNa}(\text{COOEt}) \cdot \text{CNa}(\text{COOEt}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ ) separates. In order to prepare *ethyl paranitrobenzoyltetramethylenecarboxylate*,  $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \\ \text{COOEt} \end{smallmatrix}$ , ethyl paranitrobenzoyl-

sodacetate (10 grams) is heated with trimethylene bromide (8 grams) and alcohol (30 grams) in a sealed tube for 3–4 hours at  $100^\circ$ ; sodium (0.9 gram) dissolved in a little absolute alcohol is added, and the heating continued for some length of time; the alcohol is then distilled off, water added, and the product extracted with ether. It forms magnificent, bright yellow, monoclinic crystals melting at  $62$ – $63^\circ$ . Paranitrobenzoyltetramethylenecarboxylic acid crystallises from benzene in short, thick prisms, melting at  $172^\circ$ ; its salts are very stable. *Ethyl allylparanitrobenzoylacetate*,



is obtained by heating ethyl paranitrobenzoylsodacetate (10 grams) with allyl iodide (11 grams) and alcohol. It melts at  $45$ – $46^\circ$ , crystallises from dilute alcohol in colourless, silky scales, and is decomposed by potash into paranitrobenzoic acid and other products. *Ethyl paranitrobenzoyltrimethylenecarboxylate*,  $< \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \\ \text{COOEt} \end{smallmatrix}$ , is produced

by heating ethyl paranitrobenzoylsodacetate (10 grams) with ethylene bromide (9 grams) and alcohol for two hours at  $100^\circ$ ; 0.5 gram sodium dissolved in absolute alcohol is then added, and the whole again heated for two hours at  $100^\circ$ . The purified product forms large, golden-yellow prisms, melting at  $84^\circ$ . Its formation takes place in the same way as that of ethyl paranitrobenzoyltetramethylenecarboxylate. The free acid crystallises in colourless needles, melting at  $176^\circ$ ; the silver salt,  $\text{C}_{11}\text{H}_8\text{NO}_5\text{Ag}$ , is obtained as a white, amorphous precipitate.

A. K. M.

**Phosphorsellinic Acid.** By H. SCHIFF (*Annalen*, 228, 56–72). —Pure orsellinic acid dissolves in phosphorus oxychloride, forming a yellow solution. If the liquid is gradually raised to a temperature of  $90^\circ$ , its colour changes to brown, violet, green, and finally indigo. When the evolution of hydrogen chloride ceases, the crude product is poured into ice-cold water. The phosphorsellinic acid is then deposited as an indigo-coloured powder. It is purified by solution in water and reprecipitation with hydrochloric acid or sodium chloride. The dry compound resembles indigo in appearance. It is soluble in alcohol and in water with an intense blue coloration. It is precipitated from



its aqueous solution by the addition of one-tenth the volume of hydrochloric acid, and also by sulphuric acid and certain salts of the alkali metals. Phosphorsellinic acid dissolves in lime and baryta-water, and in solutions of the caustic alkalis, yielding a soluble salt of a violet-red colour. With a solution of basic lead acetate, phosphorsellinic acid produces a violet precipitate of the composition  $C_{40}H_{22}Pb_7P_4O_{24}$ . If this precipitate is digested with a solution of basic lead acetate, it is converted into a greyish-violet basic salt,  $C_{40}H_{25}(Pb \cdot OH)_{11}P_4O_{24}$ . *Acetophosphorsellinic acid*,  $C_{40}H_{33}Ac_3P_4O_{24}$ , yields an amorphous lead salt,  $C_{10}H_{25}Ac_3(Pb \cdot OH)_3P_4O_{24}$ .

Boiling aniline dissolves phosphorsellinic acid, and converts it into an anilide,  $C_{40}H_{31}(NHPh)_2P_4O_{22}$ , which is soluble in alkalis, and unites with metals to form salts.

*Paraphosphorsellinic acid*,  $P_2(C_8H_8O_4)_5$ , is a green powder, less soluble in water than the blue phosphorsellinic acid. The salts which the metals of the alkalis and lead form with this acid are yellow in colour.

W. C. W.

**An Amide of Gallic Acid.** By H. SCHIFF and E. PONS (*Ber.*, **18**, 487—490).—The authors refer to the preparation of gallamide by the action of ammonia on tannin in an atmosphere of hydrogen, &c. (see Schiff, *Abstr.*, 1883, 335, and Etti, 1884, 1355), but they prefer the older method of Knop, who employed ammonium sulphite. Knop's formula,  $C_6H_2(OH)_3CO \cdot NH_2 + 1\frac{1}{2}H_2O$ , for gallamide is confirmed. When anhydrous, it melts at  $243^\circ$ , and decomposes at  $245^\circ$  with evolution of gas. An *acetyl*-derivative,  $C_6H_2(OAc)_3CONH_2$ , has been obtained, and forms nodular crystals which are stable in a vacuum, but change colour on exposure to the air; it does not melt sharply, but is completely liquid at  $150^\circ$ ; it is soluble in alcohol, acetic acid, and in water, sparingly in boiling benzene, and is almost insoluble in ether and chloroform. When heated with sulphuric acid and a few drops of alcohol, ethyl acetate is produced, whilst with sulphuric acid alone it yields rufigallic acid. A copper-derivative of gallamide,  $HO \cdot C_6H_2(O_2Cu) \cdot CONH_2$ , is obtained by precipitating an alcoholic solution with alcoholic copper acetate. An attempt to prepare the corresponding lead compound gave a product which appeared to be a mixture of  $C_7H_5PbNO_4$  and  $(C_7H_4NO_4)_2Pb_3$ . On treating the metallic derivatives with ethyl iodide, no characteristic products could be obtained.

Gallamide dissolves in warm benzaldehyde, and reacts with it above  $150^\circ$  with separation of water; on heating the product with an acid, benzaldehyde is re-formed. Resinous products are obtained by the action of chloroform on alkaline solutions of gallamide.

A. K. M.

**Phthalylaspartic Acid.** By A. PIUTTI (*Gazzetta*, **14**, 473—478).—Phthalic anhydride forms with aspartic acid *phthalylaspartic acid*,  $COOH \cdot CH_2 \cdot CH(COOH)N : C_2O_2 \cdot C_6H_4$ , with elimination of 1 mol.  $H_2O$ . This substance crystallises in tufts of prisms, melting at  $233^\circ$ ; it is decomposed into its constituents when heated with hydrochloric acid; by the prolonged action of aniline it is converted into *phenylphthalimide* and *phenylaspartic phenylimide*, the latter of which crystallises in glistening needles, melting at  $263^\circ$ .

By the action of diphenylamine on phthalylaspartic acid two isomeric *phthalyl*diphenylasparagines,  $\text{CONPh}_2 \cdot \text{C}_2\text{H}_4(\text{COOH}) \cdot \text{N} : \text{C}_2\text{O}_2 : \text{C}_6\text{H}_4$ , are produced, and can be separated from one another by fractional crystallisation from alcohol. One of the modifications crystallises in tufts of needles containing 2 mols.  $\text{H}_2\text{O}$ , and melts at  $112^\circ$ , but when anhydrous at  $180^\circ$ ; its silver salt is precipitated in the flocculent form but becomes crystalline; it is decomposed by the action of ammonia without forming a stable salt. The other modification crystallises in rhombic prisms which melt at  $203^\circ$ , its silver salt forms an indistinctly crystalline mass; an ammonium salt, stable at  $100^\circ$ , can be obtained. The former, when decomposed by ammonia, yields diphenylasparagine,  $\text{CONPh}_2 \cdot \text{C}_2\text{H}_4(\text{NH}_2) \cdot \text{COOH}$ , together with *phthalyl*diphenylaminaspartein, crystallising in long silky needles, melting at  $273^\circ$ , the nitro-derivative of which forms a violet potassium salt, decomposed by water; the *phthalyl*diphenylaminaspartein is also produced by heating the *phthalyl*diphenylasparagine. In like manner, the modification melting at  $203^\circ$  yields an aspartein, but the quantity of substance at the author's disposal was too small to determine whether it was identical or isomeric with the aspartein described above.

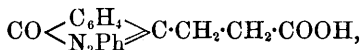
V. H. V.

**Phthalyl-derivatives.** By W. ROSER (*Ber.*, 18, 802—806).—By the action of phenylhydrazine on benzoylacetocarboxylic acid, the compound  $\text{CO} < \text{C}_6\text{H}_4 / \text{N}_2\text{Ph} > \text{C} \cdot \text{CH}_2 \cdot \text{COOH}$  is obtained, together with the phenylhydrazine compound of acetophenonecarboxylic acid. The former crystallises in lustrous plates, melts at  $160^\circ$  with evolution of carbonic anhydride, is sparingly soluble in water, readily soluble in alcohol and alkalis, and behaves as an acid. The calcium salt,  $(\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_3)_2\text{Ca} + 3\text{H}_2\text{O}$ , crystallises in matted needles; the barium and silver salts are also described.

*Acetophenonecarboxylic phenylhydrazide*,  $\text{C}_{15}\text{H}_{12}\text{ON}_2$ , crystallises in tables or prisms, melts at  $102^\circ$ , and is readily soluble in alcohol.

*Ethylenebenzoylcarboxylic phenylhydrazide*,  $\text{C}_{30}\text{H}_{22}\text{N}_4\text{O}_2$ , crystallises in short prisms, melts at  $236$ — $237^\circ$ , and is insoluble in water, sparingly soluble in alcohol, readily soluble in acetic acid.

*Phenylhydrazine- $\beta$ -benzoylpropio-orthocarboxylic acid*,



is prepared by the action of phenylhydrazine on the double lactone derived from the acid. It crystallises in needles, melts at  $210^\circ$ , and yields well-characterised salts. The calcium salt,  $(\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_3)_2\text{Ca} + 3\text{H}_2\text{O}$ , crystallises in needles; the silver and barium salts are also described.

The phenylhydrazine compound of orthobenzoylbenzoic acid,  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}$ , forms small needles, melts at  $180$ — $182^\circ$ , is sparingly soluble in alcohol, insoluble in water and aqueous soda.

A. J. G.

**Diphthalyl.** By C. GRAEBE and H. SCHMALZIGAUG (*Annalen*, 228, 126—140).—In a previous communication (*Abstr.*, 1882, 1298), the authors pointed out that diphthalyl is a dilactone, and that its vapour-

density agrees with the formula  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{C} : \text{C} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{CO}$ . The substance which Ador (*Annalen*, 164, 229) obtained by the action of phosphorus pentachloride on diphthalyl is an additive, not a substitution product. This chloride is analogous to the bromide  $\text{C}_{16}\text{H}_8\text{O}_4\text{Br}_2$ , previously described by the authors (*loc. cit.*). It melts at  $245^\circ$ , and is soluble in chloroform.

*Diphthalyl lactonic acid*,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{C} : \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , is formed on warming diphthalyl with alcoholic potash in a flask from which the air is excluded. On the addition of hydrochloric acid, diphthalyl lactonic acid is precipitated. The acid decomposes between  $200^\circ$  and  $220^\circ$ , yielding diphthalyl. It dissolves in alkalis, and the solutions rapidly oxidise on exposure to the air, forming diphthalic acid.

A solution of ammonium diphthalyl lactonate is decomposed by heat, and a substance of the composition  $\text{C}_{16}\text{H}_8\text{NO}_3$  is deposited. This compound is soluble in alcohol, ether, chloroform, and in hot acetic acid.

On reduction with zinc-dust in alkaline solution, diphthalyl yields the hydrodiphthalyl lactonic acid, which Wislicenus (this vol., p. 57) recently obtained from phthalic anhydride. W. C. W.

**The Constitution of Isumvic Acid.** By J. SCHREDER (*Monatsh. Chem.*, 6, 168—171).—When this acid is oxidised with potassium permanganate, it yields orthophthalic acid; consequently isumvic acid contains not three, but two side chains, and these in the ortho-position; this is further proved by fusing isumvic acid with potash, when orthotoluic acid is obtained. These results show that isumvic acid is identical with the phenylacetorthocarboxylic acid prepared by Wislicenus (this vol., p. 532). H. B.

**Action of Phenylhydrazine on Sulphinic Acids.** By R. ESCALES (*Ber.*, 18, 893—898).—When an aqueous solution of phenylhydrazine hydrochloride is heated on a water-bath with benzenesulphinic acid, crystals separate out, which consist of a mixture of *benzene disulphoxide*,  $\text{PhS} \cdot \text{SO}_2\text{Ph}$ , and *phenylbenzene sulphazide*,  $\text{NHPh} \cdot \text{NHSO}_2\text{Ph}$ , identical with that described by Fischer (*Abstr.*, 1878, 309) and Koenigs (*ibid.*, 219). These compounds are easily separated, the former being soluble in ether, whilst the latter is insoluble. The reaction is analogous to the decomposition of benzenesulphinic acid under similar conditions into benzene disulphoxide and benzenesulphonic acid.

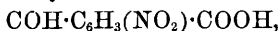
*Phenylhydrazine benzenesulphinate* is formed by mixing ethereal solutions of phenylhydrazine and benzenesulphinic acid. It crystallises from water in thin shining leaflets melting at  $130$ — $131^\circ$ . It is soluble in hot water and sparingly soluble in hot alcohol, but insoluble in ether, chloroform, and carbon bisulphide.

Phenylbenzene sulphazide and sodic hydroxide reduce Fehling's solution in the cold. When this compound is heated with sodium hydroxide, it is resolved into sodium benzenesulphinate, benzene, and nitrogen.

Sodium ethylate reacts with an alcoholic solution of phenylbenzenesulphazide, forming the compound  $C_{12}H_{11}NaN_2SO_2$ , which decomposes spontaneously. P. P. B.

**Dry Distillation of Ammonium Benzenesulphonate.** By K. EGLI (*Ber.*, **18**, 575—577).—Besides benzene, a small quantity of a high boiling oil is always obtained. This oil contains benzenesulphonamide, diphenyl, phenyl sulphide, diphenyl sulphone, phenylmercaptan, and traces of quinoline. (See also Stenhouse, *Proc. Roy. Soc.*, **14**, 351.) L. T. T.

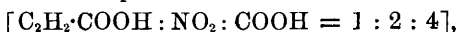
**Indigodicarboxylic Acid.** By W. Löw (*Ber.*, **18**, 947—951).—*Terephthalaldehydic acid*,  $COH \cdot C_6H_4 \cdot COOH$ , is obtained on oxidising terephthalic aldehyde with the calculated quantity of chromic mixture. It crystallises in needles melting at  $255^\circ$ , and is sparingly soluble in ether, chloroform, and hot water. The ethyl salt forms clusters of spear-shaped crystals. The *nitro-derivative*,



may be prepared by treating a solution of terephthalaldehydic acid in concentrated sulphuric acid at  $105^\circ$  with a sulphuric acid solution of potassium nitrate. The product crystallises in large, four-sided, needle-shaped prisms melting at  $160^\circ$ , is readily soluble in ether and alcohol, sparingly in chloroform; the ethyl salt is an oil. By the action of sodium acetate and acetic anhydride on the ethyl-derivative of terephthalaldehydic acid, the ethyl-derivative (m. p.  $220^\circ$ ) of *paracarboxylcinnamic acid* is produced. The free acid,



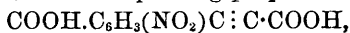
does not melt, is sparingly soluble in boiling glacial acetic acid, and nearly insoluble in the ordinary solvents; it crystallises in scales. At  $100^\circ$ , the carboxylcinnamic acid takes up bromine, with formation of *carboxyldibromocinnamic acid*,  $COOH \cdot C_6H_4 \cdot CHBr \cdot CHBr \cdot COOH$ , which is very readily soluble in methyl alcohol; it decomposes above  $300^\circ$  without melting. On nitrating carboxylcinnamic acid with a mixture of nitric and sulphuric acids, a *nitro-acid*,



is obtained, which crystallises in needles melting at  $287^\circ$  with decomposition; this yields a *carboxylnitrodibromocinnamic acid*,

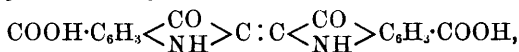


which decomposes at  $220^\circ$ . On treating the last acid with concentrated soda solution, the corresponding propiolic acid,



is produced.

Nitroterephthalaldehydic acid,  $[COH : NO_2 : COOH = 1 : 2 : 4]$ , is condensed with acetone and aqueous soda, and the diluted liquid heated for 1—2 hours at  $50^\circ$ . On adding dilute sulphuric acid to the dark green product, *indigodicarboxylic acid*,



is thrown down as a deep blue precipitate, which has an intense coppery lustre when washed and dried. It may also be obtained by dissolving carboxylnitrophenylpropionic acid in sodium carbonate solution, and heating with grape-sugar and soda. Indigodicarboxylic acid is insoluble in chloroform, ether, and alcohol, and forms a deep blue solution with concentrated sulphuric acid, from which it is reprecipitated on dilution. It dissolves in alkalis to a blue-green solution, which shows the indigo spectrum, but with the characteristic bright band displaced towards the red. The metallic salts exhibit different shades of green and blue, the silver salt being, however, brown. The barium salt has the formula  $C_{16}H_8N_2O_6Ba$ . The silver salt is found to contain 4 atoms of silver in the molecule, showing that not only the carboxyl, but also the imidic hydrogen-atoms are substituted. The ethyl salt is obtained by the condensation of the ethyl-derivative of nitroterephthalaldehydic acid with acetone and soda. It is almost insoluble in alcohol and ether, sparingly in benzene and chloroform; it dissolves in concentrated sulphuric acid with deep blue colour, and on the addition of water separates, but becomes partly saponified. A. K. M.

**Nitration-products of Diphenylethane.** By R. ANSCHÜTZ and C. ROMIG (*Ber.*, 18, 935—936).—Certain derivatives obtained by the action of nitric acid on diphenylethane dissolved in glacial acetic acid (this vol., p. 768) were assumed to contain the nitro-groups in the place of hydrogen in the benzene nucleus. It is found, however, that by the oxidation of these so-called mono- and di-nitrodiphenylethanes, *benzophenone* is produced, and not the expected nitrobenzophenones. It is therefore probable that the nitration (if it be nitration) takes place in the ethylidene-group, and that the formulæ of the mononitrodiphenylethane and dinitrodiphenylethane are  $Ph_2C_2H_3 \cdot NO_2$  and  $Ph_2C_2H_2(NO_2)_2$  respectively. The oxidation of mononitrodiphenyl carbinol and of mononitrodiphenylethylene has not yet been carried out.

A. K. M.

**Action of Potassium Nitrite and Phenols on Diamidotriphenylmethane.** By G. MAZZARA (*Guzzetta*, 14, 510—515).—With a view of preparing complex diazo-derivatives, diamidotriphenylmethane hydrochloride was treated with potassium nitrite in the presence of phenol. A reddish-brown, amorphous precipitate was produced soluble in potash to form a red liquid, and reprecipitated by acids. The numbers obtained on analysis were intermediate between those required by the formula  $C_{50}H_{39}N_3O_4$  and  $C_{28}H_{21}N_3O_2$ . The potassium salt derived from it by the displacement of two proportions of hydrogen by potassium is a reddish-brown substance, decomposing when dry, and is then insoluble in water. Its silver salt is a reddish-brown, amorphous precipitate. Of the above formulæ, the author gives preference to the latter, which corresponds with that of an amidodiazod-derivative,  $NH_2 \cdot C_6H_4 \cdot CPh(OH) \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OH$ , so that the behaviour of diamidotriphenylmethane would seem to be analogous to that of the diamidobenzoic acids and paraphenylenediamine.

V. H. V.

**Amido- and Hydroxy-derivatives of Phenylacridine.** By W. HESS and A. BERNTHSEN (*Ber.*, 18, 689—699).—A continuation of

Bernthsen's researches on this subject (Abstr., 1883, 580, 1099, 1133, 1134; 1884, 1356, 1357).

*Phenylamidoacridine*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} \diagdown \\ | \\ \text{CPh} \end{array} \text{C}_6\text{H}_3\cdot\text{NH}_2$  [ $\text{NH}_2 = 3$ ], is pre-

pared by heating a mixture of paramidodiphenylamine (1 mol.), benzoic acid (2 mols.), and an equal weight of zinc chloride, first for eight hours at  $220\text{--}230^\circ$ , and then for two to three hours at  $240\text{--}250^\circ$ ; the fused mass is extracted with ammonia, the residue boiled with hydrochloric acid, and the acid solution neutralised, when a voluminous yellow flocculent precipitate of the new base is obtained. It cannot be crystallised; it is soluble in benzene and ether, the solutions showing a green fluorescence. The salts do not crystallise, and their solutions are scarcely fluorescent. A crystalline acetyl-derivative was obtained. When treated with zinc and hydrochloric acid, two hydro-compounds are formed, the one crystallises in silvery plates, turns brown at  $181^\circ$ , is completely fused at  $192^\circ$ , and has basic properties; the other is not a base, is crystalline, and melts at  $155\text{--}160^\circ$ .

*Phenylhydroxyacridine*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} \diagdown \\ | \\ \text{CPh} \end{array} \text{C}_6\text{H}_3\cdot\text{OH}$ , is formed in small

quantity by heating parahydroxydiphenylamine with benzoic acid and zinc chloride, or better, by heating phenylamidoacridine with excess of hydrochloric acid at  $200\text{--}220^\circ$ . It crystallises in thin yellow tables or prisms, begins to turn brown at  $260^\circ$ , but is not completely melted at  $275^\circ$ ; it is readily soluble in alcohol and glacial acetic acid, soluble in ether, but only sparingly in benzene and chloroform; the alcoholic and ethereal solutions show a pale blue fluorescence. It has the properties both of a base and a phenol. The hydrochloride forms small crystals, but is more usually obtained as a jelly. The platinumchloride forms small, red crystals. If heated with acetic anhydride, it yields *phenylacetoxyacridine*,  $\text{C}_6\text{H}_4:\text{NCPh}:\text{C}_6\text{H}_3\cdot\text{OAc}$ , crystallising in tetragonal prisms and melting at  $173\text{--}174^\circ$ .

Attempts to prepare phenylacridines in which substitution occurs in the phenyl-group have not so far been very successful, although an

*amidophenylacridine*,  $\text{N} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , seems to be formed in

small quantity, together with acridine, by heating a mixture of paramidobenzoic acid, diphenylamine, and zinc chloride. It crystallises in small, yellow prisms, melts at  $215\text{--}220^\circ$ , and yields salts whose solutions have a bluish-green fluorescence. A. J. G.

**Preparation of the Nitrosonaphthols.** By R. HENRIQUES and M. LLINSKI (*Ber.*, 18, 704—706).—The following methods give much larger yields of the nitrosonaphthols than are obtained by the earlier methods:—1 part of  $\beta$ -naphthol and 0.75 part of zinc chloride are dissolved in 6 parts of alcohol, and a concentrated aqueous solution 0.5 part of sodium nitrite added to the boiling liquid; after remaining for some time, the separated zinc salt of  $\beta$ -nitrosonaphthol is

decomposed by digestion with aqueous soda; the sodium salt so obtained is washed with a little cold water, and decomposed with moderately concentrated hydrochloric acid, when nitroso- $\beta$ -naphthol is obtained nearly pure.

A solution of 1 part  $\alpha$ -naphthol, 1 part zinc chloride, and 6 parts alcohol is heated to boiling, 0.5 part sodium nitrite added, the mixture boiled for two to three hours, and then left to itself for some time. A mixture of  $\alpha$ -nitroso- $\alpha$ -naphthol with the zinc salt of  $\beta$ -nitroso- $\alpha$ -naphthol is obtained, from which the  $\alpha$ -nitroso- $\alpha$ -naphthol, together with any unaltered  $\alpha$ -naphthol, is extracted by alcoholic potash. On diluting the solution with 3—4 vols. of water,  $\alpha$ -nitroso- $\alpha$ -naphthol separates first, and can be finally purified by washing with cold benzene, in which it is only sparingly soluble. A. J. G.

**Behaviour of  $\alpha$ -Naphthaquinone and Benzoquinone towards Sulphuric Acid.** By C. LIEBERMANN (*Ber.*, 18, 966—968).—When  $\alpha$ -naphthaquinone is steam-distilled with sulphuric acid, a considerable quantity of a greyish-violet non-volatile substance is produced. This reaction is thought to be related to that of Stenhouse and Groves (*Trans.*, 1878, 417) by which dinaphthyldiquinhydrone is obtained from  $\beta$ -naphthaquinone.

When finely powdered benzoquinone is treated with dilute sulphuric acid, a yellow solution is obtained, which soon darkens in colour and deposits a mass of brownish-violet flakes. The same effect is produced by the action of a few drops of concentrated sulphuric acid on a solution of quinone in glacial acetic acid.

The condensation-product from  $\alpha$ -naphthaquinone forms an insoluble powder which does not melt at 270°. It is reduced by zinc-dust in glacial acetic and hydrochloric acids to a colourless compound, the acetyl-derivative of which crystallises from aniline in slender needles. Chromic acid converts it into an insoluble orange-coloured substance and nitric acid into the brick-red quinone. The quinone and the original condensation-product yield an abundance of phthalic acid when treated with permanganate. When the condensation-product is passed over ignited zinc-dust, a high boiling distillate is obtained containing dinaphthyl and other compounds.

The condensation-product from benzoquinone is sparingly soluble in glacial acetic acid, readily in boiling alcohol, the solution showing a dark blue fluorescence. It does not melt at 250°, and when distilled with zinc-dust, it yields a difficultly volatile liquid and a white crystalline solid substance, the latter having an odour resembling that of diphenyl. A. K. M.

[*Note*.—The formation of these condensation-products from  $\alpha$ -naphthaquinone and benzoquinone was mentioned in the paper by Stenhouse and Groves referred to (*Trans.*, 1878, 422).—EDITOR.]

**Action of Diazo-compounds on  $\beta$ -Naphthylamine.** By T. A. LAWSON (*Ber.*, 18, 796—802).—The product of the action of metanitrodiazobenzene on  $\beta$ -naphthylamine, obtained by Meldola (*Trans.*, 1884, 107), and that obtained by Griess by the action of diazobenzenesulphonic acid on the same base (*Abstr.*, 1883, 180 and 1102), as also a

compound prepared by the author by the action of diazobenzene on naphthylamine all give off nitrogen and yield salts of naphthylamine when heated with acids, and are therefore probably diazoamido-compounds. These substances, however, form acetyl- and benzoyl-compounds, which is not the case with most diazo-compounds. With reducing agents they behave as amidoazo-compounds; they do not yield hydrazine-compounds, but a naphthalenediamine.

*Diazobenene-β-naphthylamine*,  $C_{10}H_7NH \cdot N_2Ph$ , is prepared by treating an alcoholic solution of β-naphthylamine with a weak alcoholic solution of diazobenzene sulphate; it crystallises in bright red rhombic tables, is readily soluble in alcohol and acetic acid, but insoluble in water; it melts between 102 and 104°, and is unaltered by heating with alcoholic potash; concentrated sulphuric acid dissolves it, forming a blue solution, from which water precipitates it unaltered. When heated with dilute sulphuric acid, it is decomposed, nitrogen being given off and β-naphthylamine re-formed. The *acetyl*-compound,  $C_{10}H_7N\overline{Ac} \cdot N_2Ph$ , is obtained by heating a solution of diazobenene-β-naphthylamine in acetic acid with a little anhydrous acetic acid; on the addition of water, the acetyl-compound is precipitated in small red needles which melt at 152—153°; it is insoluble in water, but readily soluble in alcohol; by long heating with alcoholic potash, it again yields diazobenene-β-naphthylamine. The *benzoyl*-compound,  $C_{10}H_7N\overline{Bz} \cdot N_2Ph$ , is obtained by melting together 1 part of diazobenene-β-naphthylamine with 2 parts of benzoic anhydride at a gentle heat; it crystallises in compact red crystals, and melts at 162—163°.

By treating an alcoholic solution of diazobenene-β-naphthylamine with stannous chloride, or with zinc-dust and acetic acid, the base prepared by Griess by acting on diazobenzenesulphonic acid with β-naphthylamine is obtained.

The *hydrochloride*,  $C_{10}H_6(NH_2)_2 \cdot 2HCl$ , is easily soluble in water, but insoluble in hydrochloric acid; it crystallises in short curved prisms. The *sulphate* is obtained in white scales on adding sulphuric acid to a solution of the base. The *picrate* is a yellow crystalline powder, almost insoluble in water. The acetyl-compound,  $C_{10}H_6(NH\overline{Ac})_2$ , crystallises in white needles, and melts at 234°. A *benzoyl*-compound,  $NH_2 \cdot C_{10}H_6 \cdot NH\overline{Bz}$ , is obtained as a crystalline powder; it melts at 280°.

A. P.

**Hydroxyjuglone.** By F. MYLIUS (*Ber.*, 18, 463—481).—The juglone employed in the following experiments was prepared by oxidising α-hydroxyjuglone (this vol., p. 169) in aqueous solution with ferric chloride. Its solutions in alkalis, ammonia, in baryta- and lime-water change colour on exposure to the air; a copper-derivative,  $(C_{10}H_5O_3)_2Cu$ , may, however, be obtained, which forms dark violet microscopic prisms, almost insoluble in water. When juglone is added to a dilute solution of dimethylamine, a violet liquid is obtained which becomes brown on exposure to the air, whilst *dimethylamido-juglone*,  $C_{10}H_5O_3 \cdot NMe_2$ , separates. This is crystallised from alcohol, and then forms brownish-violet plates melting at 149—150°; it is insoluble in water, sparingly soluble in cold alcohol, ether, light



petroleum, and glacial acetic acid, more readily on warming, and very readily soluble in chloroform, benzene, and carbon bisulphide. It yields a purple-red solution with concentrated sulphuric acid, from which it is precipitated unchanged on the addition of water; it is almost insoluble in alkalis and in ammonia. When bromine is added to its solution in chloroform, an unstable yellow additive compound is precipitated. On warming an alcoholic solution of dimethylamidojuglone with stannous chloride, and then precipitating the tin as sulphide, a solution containing dimethylamidohydrojuglone hydrochloride is obtained, from which the original substance may be reproduced by atmospheric oxidation, or by means of ferric chloride. Dimethylamidojuglone is insoluble in dilute but soluble in concentrated hydrochloric acid to a purple-red solution; this is decomposed by heat with formation of hydroxyjuglone and dimethylamine. *Hydroxyjuglone* forms gold-coloured needles, almost insoluble in water and light petroleum, sparingly soluble in alcohol, ether, benzene, and carbon bisulphide, readily in chloroform and acetone; it darkens above  $200^{\circ}$ , and about  $220^{\circ}$  it decomposes with evolution of gas; it may be sublimed by careful heating, its vapour emitting an odour recalling that of juglone.

The resemblance of juglone to quinone led the author to try the action of dimethylamine on the latter; this reaction yields the compound  $C_6H_2O_2(NMe_2)_2$  which melts at  $173-174^{\circ}$ , and is decomposed when heated with concentrated hydrochloric acid, with production of dimethylamine and an acid substance crystallising in yellow rhombs, and which may be assumed to be dihydroxyquinone.

Hydroxyjuglone may be prepared by the oxidation of juglone in alkaline solution either by atmospheric oxygen or by potassium ferricyanide. It yields a cherry-red solution with concentrated sulphuric acid, and on warming its alcoholic solution with stannous chloride, it is readily reduced to a hydroquinone. Hydroxyjuglone is strongly acid, and yields well-characterised salts; the sodium salt,  $C_{10}H_4O_4Na_2$ , forms brick-red needles; other normal salts have been prepared, whilst hydrogen metallic salts also appear to exist. The dibasicity of hydroxyjuglone is further proved by the production of the *benzoyl-derivative*,  $C_{10}H_4O_4Bz_2$ ; this forms small yellowish-white granular crystals melting at  $169-170^{\circ}$ , is insoluble in water, sparingly soluble in alcohol and glacial acetic acid, but readily in benzene. When hydroxyjuglone in alcoholic solution is heated with aniline, *anilidojuglone*,  $C_{10}H_5O_3 \cdot NHPh$ , is obtained, crystallising in red, rectangular plates melting at  $230^{\circ}$ ; it dissolves in sulphuric acid with purple coloration, and in concentrated hydrochloric acid with red coloration. On boiling this solution, aniline and hydroxyjuglone are reproduced. Anilidojuglone dissolves sparingly in alkalis to a purple-red solution from which acids reprecipitate it. When juglone is oxidised in an acid solution, no hydroxyjuglone is produced. It is decomposed by an alkaline solution of bromine with formation of carbon tetrabromide. It dissolves unchanged in fuming nitric acid, but it is decomposed when the solution is boiled; it is also slowly attacked by a hot solution of potassium dichromate in acetic acid. When juglone is boiled with water, it darkens in colour, whilst finally an amorphous greenish-

brown mass is formed, insoluble in water, and in nearly all other indifferent solvents; its composition appears to be  $C_{20}H_{10}O_7$ , so that it is not identical with Phipson's regianic acid (*Compt. rend.*, 69, 1372). When heated, this substance carbonises without melting; it dissolves in alkalis with a deep violet colour, which is not destroyed by exposure to the air; the sodium-derivative,  $C_{20}H_7O_7Na_3$ , is obtained as a violet amorphous precipitate. With concentrated sulphuric acid, it gives a red solution; the violet alkaline solutions are decolorised by stannous chloride; these properties indicate that the compound is a quinone. When  $\alpha$ -hydrojuglone is fused with 6—8 parts of potash, the following substances are produced: metahydroxybenzoic acid (chief product), phenol, salicylic acid, catechol, and a sparingly soluble acid of unknown composition.

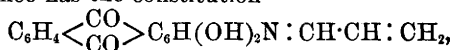
Hydrojuglone, juglone, and hydroxyjuglone, correspond with  $\alpha$ -hydronaphthaquinone,  $\alpha$ -naphthaquinone, and hydroxynaphthaquinone, of which they are the hydroxyl-derivatives. Whilst the hydroxynaphthaquinone obtained by the oxidation of naphthaquinone is a strong acid, the isomeride juglone behaves as a phenol, but assumes acid properties by conversion into hydroxyjuglone. With regard to the constitution of juglone and its derivatives, the author agrees with the views held by Bernthsen and Semper (this vol., p. 548); he suggests for  $\alpha$ -hydrojuglone the constitution  $[OH:OH:OH = 2':1:4]$ , for juglone  $[OH:O:O = 2':1:4]$ , and for hydroxyjuglone  $[OH:O:OH:O = 2':1:2:4]$ , which formulæ, however, admit of variation.

*Pipitzahoic Acid.*—This substance, to which the formula  $C_{15}H_{20}O_3$  has been assigned, was obtained by Liebig and analysed by Weld (*Annalen*, 95, 188; see also *Pharm. Zeit.*, 1883, No. 77). It is apparently a quinone, and forms gold-coloured scales melting at  $106-107^\circ$ , which sublime without decomposition, the vapour having an odour recalling that of quinone. It yields a scarlet coloration with sulphuric acid, which, however, soon disappears. The yellow alcoholic solution is decolorised by stannous chloride, and the resulting hydroquinone, which is insoluble in water, can be readily oxidised back to the quinone by the addition of ferric chloride. It yields violet solutions with the alkalis; the ammoniacal solution is decomposed, however, on evaporation, the ammonia being expelled, whilst the quinone remains behind; from this it may be concluded that pipitzahoic acid is not a true acid but a hydroxyquinone, like juglone. With aniline it yields a compound crystallising in blue needles; this gives a blue solution with concentrated sulphuric acid, but is decomposed when warmed with concentrated hydrochloric acid. It also appears to react with hydroxylamine, but is readily decomposed by bromine-water or nitric acid. On fusing pipitzahoic acid with potash, two acids are produced, one of which forms a sparingly soluble oil, and is evidently a fatty acid, whilst the other is solid and soluble in water. This result leads to the assumption that the compound  $C_{15}H_{20}O_3$  may be derived from a hydroxyquinone in which one hydrogen-atom is replaced by an unsaturated hydrocarbon-group, thus:

A. K. M.

**Remarkable Formation of Anthracene.** By H. KÖHLER (*Ber.*, **18**, 859—861).—In support of the opinion expressed by Schulze (this vol., p. 667) that the higher hydrocarbons obtained from tar owe their presence to a subsequent decomposition of phenols, which he regards as primary products of the distillation of coal, the author cites a case in which anthracene was obtained in distilling cresol. Its formation, he considers, is explained by a decomposition of the phenols, arising from a local heating of the retort. P. P. B.

**$\beta$ -Amidoalizarin.** By H. BRUNNER and E. CHUARD (*Ber.*, **18**, 445—447).—In the hope of obtaining compounds analogous to alizarin-blue,  $\beta$ -nitroalizarin was heated with concentrated sulphuric acid, and the following substances, erythrol, mannitol, glucose, and saccharose, but in all cases  $\beta$ -amidoalizarin, was produced. The different behaviour of these substances from that of glycerol suggests that the group  $C_3H_5$  causes the formation of the alizarin-blue, and that this latter substance has the constitution



proposed by Auerbach. But alizarin-blue is not obtained from amidoalizarin and acraldehyde, and when concentrated sulphuric acid acts on allyl alcohol and nitroalizarin, acraldehyde and amidoalizarin are produced. This result supports Graebe's view of the constitution of alizarin-blue:  $C_6H_4 \begin{smallmatrix} \text{CO} \\ < > \end{smallmatrix} C_6(OH)_2 \begin{smallmatrix} \text{CH:CH} \\ < \text{N:CH} > \end{smallmatrix}$  (Abstr., 1880, 262).

On heating nitroalizarin with allyl alcohol and *dilute* sulphuric acid, a product is obtained which consists essentially of amidoalizarin, but behaves in many respects like a mixture of this substance with alizarin-blue. A. K. M.

**An Isomeric Monochloro-monobromo-camphor.** By P. CAZENEUVE (*Compt. rend.*, **100**, 859—860).—When monochloro-camphor (1 mol.) is heated with bromine (2 mols.) in a sealed tube at  $110^\circ$  for one hour only instead of five, and the product washed with water and cooled, it yields a crystalline mass, which, when purified by solution in alcohol, reprecipitation by adding water, and recrystallisation from alcohol, has the composition  $C_{10}H_{14}ClBrO$ . It forms small, white, badly-defined crystals, which become brown when exposed to light if they have not been completely purified. They are very soluble in cold alcohol, ether, and chloroform, but insoluble in water.

This compound is isomeric with the monochloro-monobromo-camphor obtained by heating monochloro-camphor with bromine for five hours (this vol., p. 668); and differs from it in its physical properties. It melts at  $50^\circ$ , and has a rotatory power  $[\alpha]_D = +51^\circ$ , whilst the compound previously described melts at  $95$ – $96^\circ$ , and has a rotatory power  $[\alpha]_D = +78^\circ$ . It cannot be distilled without decomposition, but blackens and gives off hydrochloric and hydrobromic acids.

All the substitution-derivatives of camphor hitherto prepared exist in two isomeric modifications, one series being distinguished by a higher melting point and the property of forming large crystals,

whilst members of the other series crystallise badly, and are soft like the original camphor. The first series is distinguished as the  $\alpha$ - and the second as the  $\beta$ -series.

C. H. B.

**Colour Reaction exhibited by Ortho-diketones.** By E. BAMBERGER (*Ber.*, 18, 865—866).—The author finds that the ortho-diketones, phenanthrenequinone, dibromoretenequinone, chrysoquinone, and benzil give with alcoholic potash a red coloration similar to that produced by retenequinone (*Abstr.*, 1884, 1040), and that the following substances, which do not contain the two carbonyl-groups in neighbouring positions, do not yield a similar coloration: anthraquinone, ethyl succinosuccinate, ethyl diacetosuccinate, and acetonylacetone.

P. P. B.

**Camphoronic Acid.** By J. KACHLER and F. V. SPITZER (*Monatsh. Chem.*, 6, 173—194).—After referring to the researches of Kissling, Hjelt (*Abstr.*, 1880, 669), and Bredt (this vol., p. 395), the authors describe their method for purifying camphoronic acid on a moderately large scale. The crude barium salt is decomposed by hot dilute sulphuric acid. On concentrating the filtrate, the acid separates out, and is further purified by boiling with nitric acid and repeated recrystallisation from water. The melting point of pure camphoronic acid,  $C_9H_{14}O_6$ , cannot be accurately determined, as the acid easily loses 1 mol.  $H_2O$ . If a tube containing the acid is plunged in sulphuric acid at  $140^\circ$ , no change takes place, and the substance may be heated to  $150$ — $158^\circ$  before melting; but if the acid is slowly heated, it will melt at  $135^\circ$ , the melting point of the compound  $C_9H_{12}O_5$ .

Camphoronic acid forms three classes of salts:  $C_9H_{13}(NH_4)O_6$  is deposited when ammonia gas is passed into an ethereal solution of the acid. This salt easily parts with a molecule of water, forming ammonium anhydrocamphoronate,  $C_9H_{11}(NH_4)O_5$ .

Salts of the second class are obtained by neutralising the acid with metallic carbonates, for example:  $C_9H_{12}(NH_4)_2O_6$ ;  $C_9H_{12}K_2O_6 + H_2O$ . The barium salt,  $C_9H_{12}BaO_6 + H_2O$ , is a crystalline body soluble in water. On heating the aqueous solution, the normal salt,  $(C_9H_{11}O_6)_2Ba$ , is precipitated, and the acid salt,  $(C_9H_{13}O_6)_2Ba$ , remains in solution.

The cadmium salt,  $C_9H_{12}CdO_6 + 6H_2O$ , forms needle-shaped crystals freely soluble in hot water. Diethyl camphoronate,  $C_9H_{12}Et_2O_6$ , is decomposed by prolonged heating at  $220^\circ$  into alcohol and  $C_9H_{11}EtO_5$ .

The normal salts of the acid have been described by Bredt (*loc. cit.*)

Anhydrocamphoronic acid,  $C_9H_{12}O_5$ , is obtained by the distillation of camphoronic acid. It forms colourless rhombic needles—

$$a : b : c :: 0.9634 : 1 : 0.817.$$

The crystals melt at  $135^\circ$ , and dissolve freely in water, alcohol, ether, and chloroform.

The ammonium salt of this acid is obtained by passing gaseous ammonia into an ethereal solution of anhydrocamphoronic acid. The salt dissolves in water yielding an acid solution. It melts at  $125^\circ$ ,

but if it is heated for some hours at  $100^{\circ}$ , it is converted into a substance which appears to be identical with Hjelt's amido-acid.

Acetic chloride converts camphoronic acid and anhydrocamphoronic acid into the compound  $C_{18}H_{22}O_6$ . This substance melts at  $173^{\circ}$ , and is insoluble in the ordinary solvents.

The chloride,  $C_9H_{11}O_4Cl$ , is formed by the action of phosphorus pentachloride on camphoronic or anhydrocamphoronic acids. It crystallises in needles melting at  $130^{\circ}$ , soluble in warm ether and alcohol.

W. C. W.

**Red Resin from *Dracæna Cinnabari*.** By J. J. DOBBIE and G. G. HENDERSON (*Trans. Roy. Soc. Edin.*, **30**, 624—629).—The results obtained in the examination of a specimen of resin from Socotra are detailed, together with those obtained in the comparative examination of other specimens of "dragon's blood" from various sources. The first-named resin appears to consist mainly of an acid of the formula  $C_{18}H_{18}O_4$ , yielding a lead salt of the formula  $(C_{18}H_{17}O_4)_2Pb$ .

A. J. G.

**Tannin from Various Plants.** By A. FRIDOLIN (*Chem. Centr.*, 1885, 62—65).—The author gives the empirical formulæ of the tannins obtained from various plants, and finds that they all closely resemble each other. In their behaviour with dilute acids, the more soluble tannins of *Nymphenæa* and *Divi-divi* which are the poorest in carbon show the greatest resemblance, whilst another group is formed by the derivatives of *Nuphar luteum* and *Myrobalans*.

J. K. C.

**Aloin.** By H. C. PLENGE (*Pharm. J. Trans.* [3], **15**, 330).—Aloes are treated with boiling water acidified with hydrochloric acid, cooled, the solution concentrated and allowed to crystallise. The crystals thus produced are mixed with much resin, some of which is removed by pressing with bibulous paper, some by crystallisation from alcohol, and the remainder by means of ethyl acetate, which dissolves the resin more readily than the aloin. In this way, on an average, Socotrine aloes yielded 3 per cent., Barbadoes aloes 9 per cent., Curaçoa aloes 7.5 per cent., and Bonare aloes 7 per cent., of aloin. But by more careful treatment a yield of about 10 per cent. of aloin was obtained from Socotrine.

D. A. L.

**Acetylpyrroline.** By G. CIAMICIAN and P. SILBER (*Ber.*, **18**, 881—882).—The production of two isomeric compounds, *acetylpyrroline* and *pseudo-acetylpyrroline*, or *pyrryl methyl ketone*, by the action of acetic anhydride on pyrroline, has already been described (*Abstr.*, 1884, 289). The former can be completely separated from its isomeride by subjecting the mixture to repeated distillation in a current of steam. It is a liquid, boiling at  $181$ — $182^{\circ}$ . Heated with acetic anhydride, acetylpyrroline, like pseudo-acetylpyrroline, yields *pyrrylene dimethyl diketone* (*Abstr.*, 1884, 1044, and this vol., p. 378).

P. P. B.

**Action of Carbonyl Chloride on the Potassium-derivative of Pyrroline.** By G. CIAMICIAN and P. MAGNAGHI (*Ber.*, **18**, 414—420). This reaction corresponds with that of acetic chloride on pyrroline (*Abstr.*, 1884, 1044). A solution of carbonyl chloride (10 grams) in benzene (50 grams) is introduced into a reflux apparatus containing potassium-pyrroline (20 grams) and ether (250 c.c.). On warming, a violent reaction sets in which should be moderated by cooling the flask: when this ceases, the whole is heated for an hour on the water-bath. The product is filtered, the residue washed with anhydrous ether, and the filtrate evaporated. When the thick and nearly black oil obtained is distilled with steam, *carbonylpyrroline*,  $\text{CO}(\text{NC}_4\text{H}_7)_2$ , comes over; this, when purified, forms large white crystals, melts at  $62\text{--}63^\circ$ , and boils at about  $238^\circ$ , without decomposition. It dissolves readily in alcohol and ether, less so in light petroleum, and is insoluble in water. Its alcoholic solution yields a dirty white precipitate with silver nitrate, which soon blackens with formation of a mirror. Aqueous hydrochloric acid has no action on carbonylpyrroline in the cold, but when heated it dissolves with partial decomposition, forming a reddish-brown solution. Boiling alkali readily decomposes carbonylpyrroline into pyrroline and carbonic anhydride. Carbonylpyrroline forms monoclinic crystals,

$$a : b : c = 1.169 : 1.0719 ; \beta = 87^\circ 10'.$$

Tetrolcarbamide, which melts at  $165\text{--}166^\circ$  (instead of at  $167^\circ$ , as previously stated, *Abstr.*, 1883, 350), also forms monoclinic crystals,  $a : b : c = 1.2515 : 1.0792 ; \beta = 89^\circ 33'$ .

The steamed residue (see above) is filtered boiling, and the resinous mass repeatedly washed with boiling water. Flakes of *dipyrrolyl ketone* or *pyrrone*,  $\text{CO}(\text{C}_4\text{NH}_7)_2$ , separate as the filtrate cools, and may be purified by crystallisation. It forms colourless tufts of needles, melting at  $160^\circ$ . It is readily soluble in alcohol, ether, and benzene, but almost insoluble in light petroleum or water. Alkalis and boiling hydrochloric acid are without action on it. When silver nitrate, together with a few drops of ammonia, are added to the alcoholic solution, the silver compound,  $\text{CO}(\text{C}_4\text{NH}_7\text{Ag})_2$ , is thrown down as a yellow precipitate. A. K. M.

**Action of Nascent Hydrogen on Methylpyrroline.** By G. CIAMICIAN and P. MAGNAGHI (*Ber.*, **18**, 725—727).—It has been shown that pyrroline unites with nascent hydrogen to form a hydropyrroline (Ciamician and Dennstedt, *Abstr.*, 1883, 1142). Under exactly similar conditions, methylpyrroline yields *hydromethylpyrroline*,  $\text{C}_4\text{NH}_5\text{Me}$ , a colourless, strongly alkaline liquid, boiling at  $79\text{--}80^\circ$ . It mixes with water in all proportions. The hydrochloride forms a deliquescent, colourless, crystalline mass. The platinumchloride crystallises in long, orange-yellow needles. The *methiodide*,  $\text{C}_4\text{NH}_5\text{Me}, \text{MeI}$ , crystallises in colourless nacreous plates, and is identical with the compound formed by the action of methyl iodide on hydropyrroline.

By the action of hydriodic acid and phosphorus on hydropyrroline, a more hydrogenised base of the formula  $\text{C}_4\text{H}_8\text{N}$  is obtained; it boils at  $82\text{--}83^\circ$ . A. J. G.

**Action of Nitric Acid on Pyrrol Methyl Ketone.** By G. CIAMICIAN and P. SILBER (*Ber.*, **18**, 413—414).—When pyrrol methyl ketone is added to fuming nitric acid cooled to  $-18^{\circ}$ , and the product poured into water at  $0^{\circ}$ , a yellow solution is obtained from which mononitropyrrol methyl ketone,  $\text{NO}_2\cdot\text{C}_4\text{NH}_3\cdot\text{COMe}$ , separates in small needles; a further quantity is obtained on extracting the solution with ether. The aqueous solution contains oxalic acid. Mononitropyrrol methyl ketone crystallises from alcohol in small, pale yellow prisms, melts at  $196$ — $197^{\circ}$ , dissolves sparingly in water but readily in alkali. When a warm aqueous solution is treated with silver nitrate, and a few drops of ammonia added, the compound—



is obtained crystallising in small, yellow needles.

A. K. M.

**Pyrrolmethylketonesulphonic Acid.** By G. CIAMICIAN and P. SILBER (*Ber.*, **18**, 879—880).—By dissolving pseudacetylpyrroline in ten times its weight of strong sulphuric acid, a sulphonic acid of pyrrol methyl ketone or pseudacetylpyrroline is formed. This acid is very unstable, its aqueous solution decomposing when heated on a water-bath, and even when evaporated in a vacuum. The barium and potassium salts have been prepared; the latter crystallises from alcohol in long, colourless needles, and has the composition



P. P. B.

**Action of Ethyl Acetobenzalacetate on Phenylhydrazine.**

By L. KNORR and A. BLANK (*Ber.*, **18**, 931—935).—These compounds react in the cold with formation of a substance,  $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$ , isomeric with ethyl methyldiphenylpyrazenecarboxylate (this vol., p. 555), which it closely resembles in its chemical and physical properties. It is therefore named *ethyl isomethyldiphenylpyrazenecarboxylate*. Benzylidenephénylhydrazine is also produced and is exclusively obtained if the mixture is heated for some hours on the water-bath. Ethyl isomethyldiphenylpyrazenecarboxylate melts at  $110^{\circ}$ , dissolves readily in chloroform, ether, benzene, toluene, carbon bisulphide, and hot alcohol, also in strong acids, but is insoluble in water and in alkali. The free acid,  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_2$ , obtained by saponifying the ether, melts at  $194^{\circ}$  with vigorous evolution of carbonic anhydride; it resembles its isomeride (*loc. cit.*) in its properties, is insoluble in water and in dilute acids, readily soluble in concentrated acids, alkalis, ether benzene, alcohol, chloroform, and carbon bisulphide; its salts with most of the heavy metals, form white sparingly soluble precipitates, whilst the salts of the alkalis and alkaline earths are readily soluble. *Isomethyldiphenylpyrazene*,  $\text{C}_{16}\text{H}_{14}\text{N}_2$ , is obtained by the action of heat on isomethyldiphenylpyrazenecarboxylic acid. It is a weak tertiary base, melting at  $47^{\circ}$  and boiling at  $365^{\circ}$  (pressure 731 mm.); it is not acted on by nitrous acid, but combines with methyl iodide to form the compound  $\text{C}_{17}\text{H}_{17}\text{N}_2\text{I}$ . It is insoluble in water and alkali, readily soluble in strong acids and in other ordinary solvents. Its salts are decomposed by water; the stannochloride and platinochloride are described.

Like its isomeride, isomethyldiphenylpyrazene in alcoholic solution is reduced by sodium; the product,  $C_{16}H_{16}N_2$ , however, does not crystallise; it distils at about  $350^\circ$  with slight decomposition, and may be distinguished from its isomeride (*loc. cit.*) by the intense blue fluorescence of its solutions and by its reaction with nitrous acid, this producing a deep blue coloration, which is destroyed by the addition of alkali. The *methiodide* of isomethyldiphenylpyrazene melts at  $192^\circ$ , and at higher temperatures breaks up into its constituents; it is sparingly soluble in cold water, insoluble in alkali, ether, benzene, toluene, and light petroleum, readily soluble in hot water, alcohol, and chloroform, and crystallises from water in slender concentrically grouped needles. The ammonium base yields a platinochloride, which crystallises in slender orange-red needles melting at  $229^\circ$ .

A. K. M.

**Monobromopyridine.** By G. CIAMICIAN and P. SILBER (*Ber.*, 18, 721—725).—Ciamician and Dennstedt have shown that potassium pyrroline, when treated with bromoform, yields a monobromopyridine apparently identical with that obtained directly from pyridine; the conversion of this bromo-derivative into pyridine was unsatisfactory, so that absolute proof of the conversion of pyrroline into pyridine was not obtained (*Abstr.*, 1882, 1214). Monobromopyridine can be more conveniently prepared by adding pyrroline to a solution of sodium ethoxide in alcohol, and then treating the mixture with bromoform in a reflux apparatus. This bromopyridine was then treated with nascent hydrogen, and the base so obtained converted into its platinochloride and compared crystallographically with pyridine platinochloride, when the complete identity of the two specimens was established.

A. J. G.

**Nitrogenous Derivatives of Chelidonic Acids.** By L. HAITINGER and A. LIEBEN (*Ber.*, 18, 929—931).—The authors have described the formation of an oxypyridine by the action of heat on chelidonic acid (*Abstr.*, 1883, 871, and 1884, 1196), but it was doubtful whether this substance contained an OH- or an NH-group. The following experiments were made to decide this question. By the action of phosphorus chloride on oxypyridine, a *chloropyridine*,  $C_6H_4ClN$ , is produced, which closely resembles pyridine in odour and general behaviour; hydriodic acid converts it into *iodopyridine* and pyridine. This is a new and important confirmation of the relation of the nitrogenous derivatives of chelidonic acids to pyridine. When chloropyridine is heated it is converted into the hydrochloride of a new base. A *methoxyypyridine* is obtained by the action of sodium methylate on chloropyridine, and is isomeric with the methylated oxypyridine from oxypyridine and methyl iodide, or from methyl-ammonchelidonic acid. Methoxyypyridine is shown by its properties

to be an ether,  $N \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{C} \cdot \text{OMe}$ , whilst in the isomeride the methyl-group must be assumed to be united to the nitrogen,  $NMe \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{CO}$ . The close analogy between the methylated



oxypyridine and oxypyridine indicates that the latter likewise contains hydrogen united to nitrogen,  $\text{NH} \begin{smallmatrix} \text{CH} : \text{CH} \\ \text{CH} : \text{CH} \end{smallmatrix} \text{CO}$ . Chloropyridine is assumed to be  $\text{N} \begin{smallmatrix} \text{CH} : \text{CH} \\ \text{CH} : \text{CH} \end{smallmatrix} \text{CCl}$ . Methoxypyridine may be converted into the isomeride by the action of heat, whilst hydriodic acid converts it into oxypyridine. A. K. M.

**New Methypiperidine ( $\beta$ -Picoline Hexahydride).** By A. HESEKIEL (*Ber.*, 18, 910—913).— $\beta$ -Picoline, prepared by Zanoni's method (*Ann. di Chim.*, 1882, 13), from acetamide, glycerol, and phosphoric anhydride, boils at  $141.5$ — $143.5^\circ$ ; it is converted into the *hexahydride* when reduced by Ladenburg's method (*Abstr.*, 1884, 1054). The author proposes the name *pipecoline* for this hexahydride. *Pipecoline hydrochloride* forms a pale yellow, almost white salt, and yields the free base when decomposed by potassium hydroxide, as a colourless oil resembling piperidine in odour; it boils at  $124$ — $126^\circ$ , and has a sp. gr.  $0.8698$  at  $0^\circ$  and  $0.8684$  at  $4^\circ$ . The vapour-density determination gave the molecular weight  $98.14$ .  $\beta$ -Picoline and  $\beta$ -pipecoline have the constitution  $[\text{N} : \text{Me} = 1 : 3]$ .

*Pipecoline iodide*,  $\text{C}_6\text{H}_{13}\text{N}.\text{HI}$ , forms long colourless needles melting at  $131^\circ$ ; with cadmium iodide it forms a crystalline precipitate of the double iodide,  $(\text{C}_6\text{H}_{13}\text{N}.\text{HI})_2.\text{CdI}_2 + \text{H}_2\text{O}$ , which melts at  $144$ — $145^\circ$ . *Pipecoline* yields no precipitate with mercuric chloride; its *platinochloride*,  $(\text{C}_6\text{H}_{13}\text{N})_2.\text{H}_2\text{PtCl}_6$ , forms orange prisms, soluble in water, and melts at  $192^\circ$ . The *aurchloride*,  $\text{C}_6\text{H}_{13}\text{N}.\text{HAuCl}_4$ , is a yellow crystalline compound, soluble in water, and melts at  $130$ — $131^\circ$ . The *picrate*,  $\text{C}_6\text{H}_{13}\text{N}.\text{C}_6\text{H}_2(\text{NO}_2)_3.\text{OH}$ , forms pale yellow prisms, which are soluble in water and in alcohol, and melt at  $136$ — $138^\circ$ .

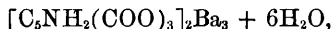
P. P. B.

**$\beta$ -Pyridinetricarboxylic Acid.** By R. VOIGT (*Annalen*, 228, 29—55).—By the action of potassium permanganate (6 mols.) on  $\beta$ -collidine (1 mol.) in a reflux apparatus,  $\beta$ -pyridinetricarboxylic acid is obtained together with lutidinemonocarboxylic and picolinedicarboxylic acids and unaltered collidine. In order to extract pure pyridinetricarboxylic acid from this mixture, the precipitated oxide of manganese is removed by filtration and extracted with hot water. The collective filtrates are concentrated and mixed with a slight excess of dilute sulphuric acid. After an interval of 24 hours the precipitate is collected, dried, and then digested with alcohol. When hydrogen chloride is passed into this alcoholic solution, the ethylic salts of pyridinetricarboxylic, lutidinemonocarboxylic, and picolinedicarboxylic acids are formed. On evaporation, ethyl pyridinetricarboxylate crystallises out, but the ethereal salts of the other acids are liquid. The crystalline mass is saponified with baryta-water and the resulting barium salt decomposed by dilute sulphuric acid. Pure  $\beta$ -pyridinetricarboxylic acid,  $\text{C}_5\text{NH}_2(\text{COOH})_3 + 2\text{H}_2\text{O}$ , forms needle-shaped crystals, freely soluble in hot water. It melts with decomposition at  $227^\circ$ . Its formation from  $\beta$ -collidine shows that it is symmetrical pyridinetricarboxylic acid. A careful comparison of this acid with

Böttlinger's  $\beta$ -pyridinetricarboxylic acid, obtained by the oxidation of uvitonic acid (Abstr., 1881, 181), shows that the acids are identical. The author, however, points out that many of Böttlinger's statements concerning this acid and its salts are incorrect.

With the exception of the magnesium and alkali salts, the normal salts of this acid are either insoluble or sparingly soluble in water. They are formed by the action of the free acid on metallic acetates, except in the case of the potassium salt, when this reaction yields the acid salt,  $C_5NH_2(COOH)_2 \cdot COOK + H_2O$ , crystallising in needles.

The normal potassium salt,  $C_5NH_2(COOK)_3 + 5H_2O$ , is deposited in needles or prisms, when alcohol is added to a mixture of potassium acetate and the neutral ammonium salt. The crystalline *calcium* salt,  $[C_5NH_2(COO)_3]_2Ca_3 + 4H_2O$ , and the amorphous *barium* salt,



are sparingly soluble. A concentrated solution of the latter salt in hydrochloric acid deposits crystals of the hydrogen barium salt,



The *magnesium* salt,  $[C_5NH_2(COO)_3]_2Mg_3 + 12H_2O$ , forms white needle-shaped crystals, freely soluble in water. The characteristic *copper* salt,  $[C_5NH_2(COO)_3]_2Cu_3 + 12H_2O$ , is sparingly soluble in water and dilute acetic acid. The *silver* salt,  $C_5NH_2(COOAg)_3 + 1\frac{1}{2}H_2O$ , is amorphous. *Ethyl pyridinetricarboxylate*,  $C_5NH_2(COOEt)_3$ , crystallises in white needles melting at  $127.5^\circ$ , which dissolve freely in ether and in hot alcohol. When treated with ammonia at  $160^\circ$ , it is converted into an amide which melts above  $280^\circ$ . It dissolves in water and alcohol. On cautious sublimation between watch-glasses, symmetrical pyridinetricarboxylic acid is converted into isonicotinic acid,  $C_5NH_4COOH$ .

The author has also investigated the pyridinedicarboxylic acid prepared from picolinemonocarboxylic acid, and he fully confirms the accuracy of Böttlinger's results. As three dicarboxylic acids are known which are decomposed by heat into carbonic anhydride and isonicotinic acid, it appears that in one case a migration of the carboxyl-group must take place during the act of decomposition.

W. C. W.

**Methochlorides of Pyridine and of Quinoline Bases.** By E. OSTERMAYER (*Ber.*, 18, 591—601; compare this vol., pp. 672, 673).—The methochlorides were obtained by saturating the base with hydrochloric acid, adding methyl alcohol, and heating the whole in sealed tubes. The compounds which they form with iodine chloride (prepared by passing a current of chlorine into water in which iodine is suspended) are especially characteristic.

*Pyridine methochloride*,  $C_5NH_5MeCl + ?H_2O$ , forms exceedingly deliquescent crystals, and could not be analysed. The *platinochloride* forms large orange-red prisms melting at  $186$ — $188^\circ$ ; the *aurochloride* crystallises from acid solutions in small needles melting at  $252$ — $253^\circ$ ; its neutral aqueous solution deposits gold when boiled. The *methopicate*,  $C_5NH_5Me \cdot O \cdot C_6H_2(NO_2)_3 + \frac{1}{2}H_2O$ , melts at  $34^\circ$ , and explodes violently at a higher temperature. It forms large, greenish-yellow

needles, which lose their water of crystallisation when exposed to the air. *Pyridine methochloride chloriodide*,  $C_5NH_5MeCl, ICl$ , forms lemon-yellow scales, soluble in hot water containing hydrochloric acid. It melts at  $81-82^\circ$ .

*Quinoline methoplatinochloride* forms yellow scales melting with decomposition at  $230^\circ$ ; the *aurochloride* is crystalline, sparingly soluble, and melts at  $205^\circ$ . When heated with zinc chloride, the methochloride yields a base,  $C_{20}N_2H_{20}O$ , crystallising in large glistening rhombic columns, and melting at  $72-75^\circ$ . It is probably an isomeride of La Coste's quinolinemethyl oxide. Its *hydrochloride* forms colourless needles melting at  $112^\circ$ ; its *platinochloride* is almost insoluble in water, and melts at  $190^\circ$ , and its *aurochloride*,  $C_{20}N_2H_{20}O, HAuCl_4$ , is also sparingly soluble.

*Dimethylamidohydroquinoline hydrochloride*,  $NMe_2 \cdot C_9NH_{11}Cl$ , was obtained by the reduction of dimethylamidoquinoline with tin and hydrochloric acid. The free base liberated by alkalis appears to be liquid, is intensely disagreeable in smell, and has a very caustic action on the skin. The *chloriodide*,  $NMe_2 \cdot C_9NH_{10}MeCl, ICl$ , forms small yellow rhombic crystals melting at  $127^\circ$ .

*Diquinoline methochloride chloriodide*,  $C_{18}N_2H_{12}Me_2Cl_2, 2ICl$ , forms pale yellow needles, very sparingly soluble in water, and melting at  $238^\circ$ .

The author points out the great similarity of these methochlorides of various bases, and their peculiar property of forming compounds with chlorine iodide. When the methiodides are brought into contact with chlorine iodide, iodine is separated and they are converted into methochlorides. The author considers that the *chloriodides* are either additive products (analogous to the dibromide previously described), or simply molecular compounds.

L. T. T.

**Alkylquinoline-derivatives.** By A. CLAUS (*Ber.*, **18**, 410—412).—A reply to Bernthsen (this vol., p. 558).

**Ammonium Bases derived from Quinoline.** By A. BERNTHSEN (*Ber.*, **18**, 1014—1018).—A reply to Claus.

**Quinoline Iodides.** By W. LA COSTE (*Ber.*, **18**, 780—785).—*Moniodoquinoline*,  $C_9NH_5I$ , may be prepared by a modification of Hlasiwetz and Weselsky's method of preparing iodo-derivatives of aromatic compounds. Pure quinoline, mixed with a little less than the theoretical amount of iodine required to form the mono-substitution-compound, mercuric oxide, and a concentrated solution of potassium iodide is heated in a sealed tube at  $160-170^\circ$ . A brown resinous mass is obtained, which becomes crystalline after a time; to isolate the iodoquinoline, this substance is heated with sulphurous anhydride in order to destroy small quantities of additive compounds formed. Excess of soda is then added and the mixture gently heated for some time, when on distillation the iodoquinoline comes over with the steam, and on cooling forms a cake of brown crystals; it is further purified by means of solution in light petroleum or alcohol, decolorised with animal charcoal, and is then allowed to crystallise. It still,

however, contains considerable quantities of unaltered quinoline, which is removed either by distillation or by treatment with dilute hydrochloric acid.

Iodoquinoline may also be easily obtained in considerable quantities by heating 6 parts of quinoline with 3 parts of iodine and 2 parts of hydriodic acid in a concentrated solution of potassium iodide at  $240^{\circ}$ ; the product obtained is very pure. This reaction yields similar products with the homologues of quinoline.

Moniodoquinoline is very soluble in ether and alcohol, less soluble in light petroleum, practically insoluble in cold water, slightly soluble in hot water. It crystallises in long, colourless, thin needles or thick prisms, melts at  $62-63^{\circ}$ , has a sp. gr. of 1.9334, is easily distilled with steam, and can be distilled alone in small quantities.

*Iodoquinoline hydrochloride*,  $C_9NH_6I.HCl + \frac{1}{2}H_2O$ , crystallises from its hydrochloric acid solution in small yellow needles. The *platinochloride*,  $(C_9NH_6I)_2.H_2PtCl_6 + 2H_2O$ , crystallises from boiling water in glistening yellow needles or tablets. *Iodoquinoline methiodide*,  $C_9NH_6I.MeI$ , crystallises in glistening, golden-yellow tablets, sparingly soluble in alcohol or cold water, readily in boiling water, practically insoluble in ether. By digesting this compound with freshly precipitated silver chloride, *iodoquinoline methochloride*,  $C_9NH_6I.MeCl$ , is obtained. It is slightly soluble in cold, but more readily in hot water; it has an intensely bitter taste, and forms a *platinochloride*,  $(C_9NH_6I.Me)_2PtCl_6$ .

*Orthiodomethylquinoline*,  $C_9NH_5.MeI$ , has been prepared in the same way as iodoquinoline; it forms small, yellowish needles, melts at  $73-74^{\circ}$ , and yields an insoluble *platinochloride*,  $(C_9NH_5.MeI)_2.H_2PtCl_6$ , crystallising in reddish-yellow needles. A. P.

**Synthetical Lutidine.** By W. EPSTEIN (*Ber.*, 18, 883).—A *lutidine* is obtained by the action of aldehyde ammonia on ethyl acetoacetate; it boils at  $145-146^{\circ}$ , forms a *platinochloride*, melting at  $216^{\circ}$ , an *aurochloride*, melting at  $119^{\circ}$ , a *picrate*, which melts at  $161^{\circ}$ , and a *dichromate* melting at  $92^{\circ}$ . The compound with mercuric chloride melts at  $155^{\circ}$ . When oxidised by potassium permanganate, it forms *isocinchomeronic acid*. P. P. B.

**Isolation of the so-called  $\alpha$ -Lutidine.** By A. LADENBURG and C. F. ROTH (*Ber.*, 18, 913—920).—In a former communication the authors described a lutidine obtained from commercial picoline. In this paper an account is given of another lutidine obtained from the bases of animal tar, and contained in the fraction boiling at  $158-160^{\circ}$ . The fraction dissolved in an excess of hydrochloric acid yields a precipitate with mercuric chloride, which is easily soluble in hot water, from which it crystallises in long, highly refractive, white needles, melting at  $130^{\circ}$ . This salt, when decomposed by caustic potash, yields the free base, which is a liquid somewhat soluble in cold water, but less soluble in hot water, and easily soluble in ether and in alcohol. It has a sp. gr. of 0.9503 at  $0^{\circ}$ . It differs from picoline, inasmuch as neither with hydrochloric acid nor benzoic chloride does it yield a red coloration. The *platinochloride*,  $(C_7NH_5)_2.H_2PtCl_6$ ,

forms orange-yellow prisms, or light yellow, shining tablets, soluble in water and melting at  $230^{\circ}$ . The *aurochloride*,  $C_7NH_9HAuCl_4$ , is obtained as an amorphous precipitate, which becomes crystalline after a time; it is sparingly soluble in water, more easily in dilute hydrochloric acid.

Lutidine, when oxidised by potassium permanganate, is converted into  $\alpha$ - $\gamma$ -pyridinecarboxylic acid. This crystallises from water in lustrous colourless leaflets, having the composition  $C_7NH_5O_4 + H_2O$ ; it is easily soluble in hot water, but only sparingly in cold water; it melts at  $235^{\circ}$ . Ether and benzene dissolve it but sparingly, alcohol more easily. Its solutions give a yellowish-red coloration with ferrous salts. The authors regard this acid as identical with Böttinger's pyridinedicarboxylic acid (Abstr., 1881, 612); also with the lutidinic acid described by Weidel and Herzig (*Monatsh.*, 1, 1). The presence of slight impurities materially affects the properties of this acid, which fact the authors consider as sufficiently explaining the difference between their observations and those of Weidel and Herzig. The following salts are described:—The *calcium* salt,  $C_7H_3NO_4Ca + H_2O$ , crystallises in leaflets; it is sparingly soluble in water; the *copper* salt forms a light blue, amorphous precipitate, which on boiling becomes crystalline; the *lead* salt is a heavy, amorphous precipitate; the *barium* salt crystallises from water in well-defined crystals; the *silver* salt is insoluble in water and is obtained as a voluminous precipitate, which becomes crystalline after a time.

This pyridinedicarboxylic acid is resolved by heat into carbonic anhydride and isonicotinic acid, the production of which shows the acid to be the  $\alpha$ - $\gamma$ -pyridinedicarboxylic acid, and consequently that the lutidine from which it is formed must be  $\alpha$ - $\gamma$ -lutidine.

$\alpha$ - $\gamma$ -Lutidine, reduced by treating its alcoholic solution with sodium, yields  $\alpha$ - $\gamma$ -hydrolutidine,  $C_7H_{15}N$ , a liquid boiling at  $140$ – $142^{\circ}$ ; it is miscible with water, alcohol, and ether, has an odour like that of the piperidine bases, and a strongly alkaline reaction; it fumes with hydrochloric acid, and has a sp. gr. of 0.8615 at  $0^{\circ}$ . The secondary character of this base is shown by its combining with carbon bisulphide and with benzoic chloride, forming a crystalline compound with the latter. Its *hydrochloride*,  $C_7H_{15}N, HCl$ , is easily soluble in water, and crystallises in long colourless needles, melting at  $235^{\circ}$ . The *hydrobromide*,  $C_7H_{15}N, HBr$ , forms easily soluble needle-shaped crystals. The *platinochloride*,  $(C_7H_{15}N)_2, H_2PtCl_6$ , crystallises in light yellow needles, and is sparingly soluble in water.

The authors have isolated naphthalene from the higher fractions of the bases of animal tar.

One of the authors proposes the following method of naming the bases homologous with piperidine:—

Pyridine,  $C_5H_5N$ .  
 Picoline,  $C_5H_4MeN$ .  
 Lutidine,  $C_5H_3Me_2N$ .  
 Collidine,  $C_6H_{11}N$ .

Piperidine,  $C_5H_{10}NH$ .  
 Pipecoline,  $C_5H_9MeNH$ .  
 Lupetidine,  $C_5H_8Me_2NH$ .  
 Copellidine,  $C_6H_{17}NH$ .

P. P. B.

**Reduction and Oxidation-products of Aldehyde-collidine.**

By C. DÜRKOPF (*Ber.*, **18**, 920—929).—Aldehyde-collidine,  $C_8H_{11}N$ , is obtained by heating ethylidene chloride (from paraldehyde) with an excess of ammonia for nine hours at  $160^\circ$ . It boils at  $176^\circ$ ; its sp. gr. is 0.9389 compared with water at  $4^\circ$ . On reducing the pure collidine by Ladenburg's method, a hexahydride (copellidine),  $C_8H_{17}N$  (*Abstr.*, 1884, 1054), is obtained, which is best purified by means of its nitroso-derivative. It boils at  $162$ — $164^\circ$ , and forms a colourless oily liquid of strongly alkaline reaction and penetrating ammoniacal odour; its physiological action is similar to that of conine, although much weaker. Its sp. gr. is 0.8653 at  $0^\circ$  and 0.8546 at  $15^\circ$ , compared with water at  $4^\circ$ . The hydrochloride, melting at  $171^\circ$ , hydrobromide,  $C_8H_{17}N \cdot HBr$ , melting at  $165^\circ$ , hydriodide, aurochloride,  $C_8H_{17}N \cdot HAuCl_4$ , melting at  $105^\circ$ , and platinochloride,  $(C_8H_{17}N)_2 \cdot H_2PtCl_6$ , melting at  $105^\circ$  or  $145$ — $147^\circ$  when dried, are described. The hexahydride reacts violently with benzoic chloride even at the ordinary temperature, a white crystalline mass being produced; it also yields an acetyl-derivative,  $C_8H_{16}N \cdot Ac$ , which forms a yellowish neutral liquid, having an odour recalling that of nicotine; its sp. gr. is 0.9787 at  $0^\circ$  and 0.9660 at  $21^\circ$ , compared with water at  $4^\circ$ . Copellidine reacts with methyl iodide with formation of *dimethylcopellidinium iodide*,  $C_8H_{16}Me_2I$ , crystallising in long white needles, and melting at  $267$ — $268^\circ$ , and *methylcopellidine*,  $C_8H_{16}NMe$ , a colourless oil boiling at  $164$ — $165^\circ$ , and having strongly alkaline properties. It is sparingly soluble in water; its sp. gr. is 0.8519 at  $0^\circ$  and 0.8440 at  $13^\circ$ , compared with water at  $4^\circ$ . Methylcopellidine closely resembles collidine; it has the odour of the pyridine bases, and has lost the penetrating smell of the hexahydride; it combines with methyl iodide with explosive violence to form dimethylcopellidinium iodide. The hydrobromide,  $C_8H_{16}NMe \cdot HBr$ , melting at  $151^\circ$ , hydrochloride, aurochloride, platinochloride, and picrate, melting at  $112^\circ$ , have been prepared, and also the platinochloride,  $(C_8H_{16}NMe_2)_2 \cdot PtCl_6$ , and mercuriochloride,  $(C_8H_{16}NMe_2)_2 \cdot HgCl_4$ , of dimethylcopellidinium. When dimethylcopellidinium iodide is treated with silver oxide and the resulting hydroxide submitted to distillation, water is eliminated and *dimethylcopellidine*,  $C_8H_{15}NMe_2$ , obtained. This is a colourless strongly alkaline liquid, boiling at  $171$ — $173^\circ$ , and of offensive odour, recalling that of trimethylamine; its sp. gr. is 0.7816 at  $25^\circ$  compared with water at  $4^\circ$ . The aurochloride and platinochloride,  $(C_8H_{15}NMe_2)_2 \cdot H_2PtCl_6$ , are described. The base combines with methyl iodide to form trimethylcopellidinium iodide.

Aldehyde-collidine is violently acted on by a boiling solution of potassium permanganate, the greater portion being oxidised to carbonic anhydride, a small quantity of pyridinecarboxylic acid being however also obtained. A better result is obtained by digesting the base for 48 hours with a 2 per cent. permanganate solution, and then heating for a short time at  $60^\circ$ . The product is a *methylpyridinecarboxylic acid*,  $C_5NH_3Me \cdot COOH$ ; it crystallises in prisms, is extremely soluble in water, and melts at  $194$ — $196^\circ$ . It is concluded from this that collidine is an ethylmethylpyridine.

A. K. M.

**Trimethylquinizine-derivatives.** By S. HALLER (*Ber.*, 18, 706—709).—These compounds were prepared from pseudocumylhydrazine by the methods described by Knorr for the preparation of quinizine compounds (*Abstr.*, 1884, 302, 1153, and 1377).

*Ethyl pseudocumylzinaacetate*,  $C_{15}H_{22}O_2N$ , crystallises in long yellow needles or prisms, melts at  $77-78^\circ$ , is sparingly soluble in cold alcohol and light petroleum, readily soluble in hot alcohol and ether. It is very unstable, soon resinifying even in closed vessels.

*Tetramethyloxyquinizine*,  $C_9NH_3Me_4O : NH$  [ $Me_4 = 1 : 3 : 4 : 2'$ ], termed  *$\psi$ -cumylmethyloxyquinizine* by the author, forms lustrous crystals melting at  $154-155^\circ$ , is sparingly soluble in water, ether, light petroleum, and alkalis, readily in alcohol and in hydrochloric acid.

*Pentamethyloxyquinizine*, ( *$\psi$ -cumylantipyrene*),  $C_9NH_3Me_4O : NMe$  [ $Me_3 : NMe : Me : O = 1 : 3 : 4 : 1', 2' : 2' : 4'$ ], crystallises in pale yellow needles, melts at  $105-106^\circ$ , is sparingly soluble in cold water and ether, readily in hot water, alcohol, benzene, and chloroform. In aqueous solution, it gives a red coloration with ferric chloride and a blue-green coloration with nitrous acid. It dissolves in pure nitric acid with deep-red colour; on adding water, the nitro-derivative separates as a rose-coloured crystalline mass. With benzaldehyde in the presence of hydrochloric acid, it yields a condensation-product crystallising in white needles.

*Isonitrosotetramethyloxyquinizine*,  $C_{12}H_{16}O_2N_3$ , crystallises in yellow needles and melts at  $156^\circ$ , is very sparingly soluble in water, readily in alcohol, ether, and hot hydrochloric and glacial acetic acids.

A. J. G.

**Reactions of Alkaloids.** By O. DE CONINCK (*Bull. Soc. Chim.*, 43, 236—247).—A continuation of the author's work on this subject (this vol., p. 671). Carbon bisulphide acts very slightly on quinoline, small transparent crystals being formed after two or three days.

Commercial cicutine, which is a mixture of cicutine and methyl-cicutine, on treatment with metallic sodium and subsequent extraction with ether, yields a sodium-derivative, which is not decomposed by water; whilst pure cicutine yields a sodium-compound from which the cicutine may be again obtained on the addition of water. Carbon bisulphide acts violently on cicutine, forming a thick brownish-yellow liquid of a disagreeable odour; on cooling, this liquid may be solidified. The platinochloride of commercial cicutine, although not altered by slow evaporation or even gentle boiling, is completely decomposed by rapid or long-continued ebullition. On dissolving this platinochloride in water, a few drops of an oily substance are always observed, which dissolve on gentle heating, but reappear on cooling. Pure cicutine platinochloride, however, dissolves quite readily in the cold, and on boiling its solution, cicutine is given off, and the platinic chloride thus set at liberty reacts on the undecomposed platinochloride, forming a blackish amorphous compound.

Nicotine is not acted on by carbon bisulphide, nor is its platinochloride altered by boiling. On treating nicotine with metallic sodium, and extracting the crystalline mass thus formed with water,

a liquid is obtained which has most of the characteristics of nicotine, but is more viscous.

If the methiodides of the pyridic alkaloids are heated with potash, a resinous compound is formed, and on adding a small quantity of water and pouring into water acidulated with hydrochloric acid, a red coloration is developed.

$\alpha$ - and  $\beta$ -collidines and analogous alkaloids yield an exceedingly characteristic odour when the methiodides are gently heated with potash; this odour is quite distinct from that observed on the similar treatment of  $\alpha$ -picoline,  $\beta$ - and  $\gamma$ -lutidines, and the pyridine-derivatives of cinchonine and brucine. The modified platinochlorides of pyridic bases obtained by boiling the normal compounds are unaltered by even the strongest hot hydrochloric acid.

Piperidine is quite unaffected by metallic sodium, no polymerisation taking place.

A. P.

**Creatines and Creatinines.** By E. DUVILLIER (*Compt. rend.*, 100, 916—917).—Cyanamide (1 mol.) and a few drops of ammonia are added to a saturated aqueous solution of  $\alpha$ -ethylamidopropionic acid (1 mol.), and the mixture allowed to stand for some months until the dicyandiamide has crystallised out. The liquid is then concentrated on a water-bath, when it deposits prismatic crystals frequently grouped in bundles. On further concentration, the liquid deposits a mixture of the prismatic crystals with rhombohedral crystals of unaltered acid. The prismatic crystals are purified by recrystallisation. They are anhydrous, and consist of  $\alpha$ -ethylamidopropionocyanidine,  $\text{HN}:\text{C} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{—} \quad \text{NEt—} \end{array} \text{CHMe}$ , soluble in alcohol, but much more soluble in water. At  $17^\circ$ , it requires 3.7 parts of water, and at  $16^\circ$  18 parts of alcohol for complete solution.

C. H. B.

**Brucine.** By A. HANSSEN (*Ber.*, 18, 777—779).—The platinochloride of the oxidation-product obtained from brucine (this vol., p. 276) is decomposed by sulphuric acid, the chlorine removed by silver oxide, and the solution evaporated to a thin syrup, when it yields brilliant crystals of the oxidation-product  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4 + 2\text{H}_2\text{O}$ ; it is unaltered in the air, but on drying at  $105^\circ$  gives up 2 mols.  $\text{H}_2\text{O}$ , and forms a porcelain-like mass. It melts at  $263$ — $264^\circ$ , with evolution of carbonic anhydride; no definite substance could be isolated from the residue. The oxidation-product is probably an acid, but definite salts have not yet been obtained. When suspended in alcohol and treated with hydrogen chloride, fine crystals of the chloride are obtained.

On heating the oxidation-product with hydrochloric acid in a sealed tube at the temperature used in separating the methoxyl-group from brucine, no gas was evolved; but on raising the temperature to  $180^\circ$ , methyl chloride was given off abundantly. Anhydrous acetic acid does not react with the oxidation-product, it therefore appears that the altered compound contains a methoxyl-group.

The ammonium base obtained from methyl brucine by treatment



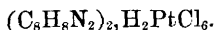
with silver oxide forms slender pale yellow crystals; it rapidly absorbs carbonic anhydride from the air, and melts at  $250\text{--}251^\circ$ . A. P.

**Preparation of Daturine from Stramonium Seed.** By J. D. A. HARTZ (*Pharm. J. Trans.* [3], 15, 203—204).—The fatty matter is first extracted by macerating and percolating the coarsely ground dry seed with light petroleum; the exhausted seed is again dried and treated a second time with petroleum, this petroleum being then used for extracting a fresh quantity of seed. In a similar manner the alkaloid is extracted by means of 60 per cent. alcohol; the extract is filtered, concentrated, treated with caustic soda, and agitated with benzene. By washing with dilute sulphuric acid, the alkaloid is removed as sulphate, which is decomposed with alkali and again agitated with benzene to dissolve the daturine. The benzene solution is filtered and allowed to crystallise. The yield is 0.167 per cent. of the dried stramonium seed. D. A. L.

**Harmine and Harmaline.** By O. FISCHER and E. TÄUBER (*Ber.*, 18, 400—406).—The method of obtaining these bases is described by Fritzsche (*Annalen*, 64, 365). Harmine crystallises from wood spirit in longish needles, melting at  $256\text{--}257^\circ$  with blackening, and sublimes with partial decomposition. Harmaline forms small yellowish plates melting at  $238^\circ$  with decomposition. The first-mentioned base yields colourless salts which, in dilute solution, exhibit an indigo-blue fluorescence, whilst the salts of the second base are coloured and resemble the acridine-derivatives in their strong fluorescence; harmalinesulphonic acid in dilute aqueous solution exhibits a splendid azure-blue fluorescence. Neither of the two bases yields either a diazo- or a nitroso-derivative. When harmaline is acted on by zinc and hydrochloric acid, a new base is produced which does give a nitroso-compound indicating that the nitrogen has become reduced. The analysis of harmine gave figures agreeing fairly with Fritzsche's formula  $C_{13}H_{12}N_2O$ , whilst the numbers obtained for harmaline deviate somewhat from the formula  $C_{13}H_{14}N_2O$ . By the action of methyl iodide on harmine, the methiodide,  $C_{13}H_{12}N_2O, MeI$ , is produced, crystallising in long needles melting at  $298^\circ$ , and is converted into the ammonium base by alkalis and by moist silver oxide. When harmine is heated with concentrated hydrochloric acid at  $140^\circ$ , methyl chloride is eliminated, and a compound, *harmol*,  $C_{12}H_{10}N_2O$ , formed, which has the properties of a phenol. It is soluble in acids and in caustic alkalis, from which it is precipitated by carbonic anhydride, is almost insoluble in water, sparingly soluble in absolute, moderately in aqueous alcohol. When gently heated with phosphorus pentachloride and oxychloride, a chloride is produced which is extremely soluble in water.

*Harminic acid*,  $C_{10}H_8N_2O_4$ , is formed by the oxidation of harmine by means of chromic acid; it is sparingly soluble in hot water and nearly insoluble in alcohol, ether, chloroform, and benzene; it darkens at  $300^\circ$ , and melts at  $345^\circ$  with evolution of carbonic anhydride and production of a crystalline sublimate of the formula  $C_8H_6N_2$ ; this is a base which is very readily soluble in alcohol and chloroform,

moderately in water, and less so in ether and benzene. It melts at  $183^{\circ}$ , and yields characteristic auro- and platino-chlorides,



The properties of this base and of harmine lead to the conclusion that the nitrogen is present in the ring-form.

Harmaline yields a methiodide,  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}, \text{MeI}$ , which is distinguished from that of harmine by its yellow colour, greater solubility, and melting point ( $260^{\circ}$ ). *Harmalol*, obtained by the action of hydrochloric acid on harmaline, forms an orange to brick-red, crystalline powder, somewhat soluble in water with a magnificent green fluorescence; it darkens at  $180^{\circ}$ , and melts at  $212^{\circ}$  with decomposition. Harmaline hydrochloride crystallises from water in small yellow needles. Harminic acid could not be obtained by the action of chromic acid on the base. The seeds of *Peganum harmala* contain (besides harmine and harmaline) a yellow colouring matter, soluble in alkalis and acids, and possibly identical with harmalol.

A. K. M.

**Constituents of Ergot of Rye.** By R. KOBERT (*Chem. Centr.*, 1885, 66—67).—Coarsely pulverised ergot of rye was extracted with ether and then with alcohol, both acidified with sulphuric acid, and finally with water. The aqueous extract was precipitated with lead acetate, filtered, and the filtrate treated with ammonia and lead acetate, which throws down the lead salt of *ergotic acid*; this was well washed and decomposed with sulphuretted hydrogen, the solution concentrated in a vacuum, and precipitated and washed with absolute alcohol. Ergotic acid is hygroscopic, and its aqueous solution gives precipitates with lime and baryta-water: it contains nitrogen. Purification with animal charcoal or fractional precipitation yields a snow-white substance which contains, however, only a trace of nitrogen. The same compound is obtained by extracting the ergot of rye directly with warm water, and is considered by the author as a carbohydrate analogous to dextrin.

*Sphacelic acid* is obtained from ergot which has been digested for 12 hours with cold dilute acid and extracted with ether, by treating it with alcohol; the alcoholic solution is precipitated with baryta, and the filtrate with sulphuric acid, the latter being removed by lead hydroxide, and the filtrate evaporated to dryness, treated with ether to dissolve fat, and then dissolved in sodium carbonate and thrown down by dilute acid. It is insoluble in water, scarcely so in ether and chloroform, easily in alcohol.

*Cornutine* is obtained from the weak acid extract by neutralising, evaporating to dryness, extracting with alcohol, and treating the residue after expulsion of the alcohol with ethyl acetate; it is removed from its solution in the latter by agitation with a weak aqueous solution of citric acid: it was not, however, obtained free from other alkaloïds.

J. K. C.

**Cornutine and Ergotinine.** By C. TANRET (*J. Pharm.* [5], 11, 309—313).—The author criticises Kobert's claim to have separated from ergot of rye in an impure state three new principles, which he

calls *ergotic acid*, *sphacelic acid*, and *cornutine* (preceding Abstract). The author complains that nothing is said about the separation of cornutine from the alkaloïds which accompany it. If an acidulated solution of ergotinine is exposed for some time to the air, it becomes more or less coloured, and finally the product which it contains gives exactly the reactions which Kobert has attributed to cornutine. Hence cornutine is only ergotinine more or less profoundly altered.

J. T.

**Behaviour of the Bile Acids with Gelatin and Gelatin Peptones.** By F. EMICH (*Monatsh. Chem.*, 6, 95—103; comp. Abstr., 1883, 673).—Glycocholic acid does not precipitate gelatin solutions, but taurocholic acid does, even from very dilute solutions, and in a very complete manner; the taurocholic acid cannot be removed from the precipitate by boiling alcohol. 1 part of gelatin combines with from 0.68 to 1.49 parts of taurocholic acid.

Taurocholic acid precipitates gelatin peptone but only incompletely. These reactions are of physiological importance.

H. B.

**Cystine.** By J. MAUTHNER (*Ber.*, 18, 451).—The statement made by the author that the substance obtained by the action of water at 140—150° on cystine does not contain nitrogen (Abstr., 1884, 1054) was founded on the negative result given by Lassaigne's test. The substance does, however, contain nitrogen, for it gives ammonia when heated with soda-lime.

A. K. M.

**Malt Peptone.** By F. SZYMANSKI (*Ber.*, 18, 492—496).—The author refers to Griessmayer's work (this Journal, 1877, ii, 521), with the results of which his own do not agree. Barley and malt are extracted with cold water, the albuminoïds coagulated by heat, the extract neutralised with very dilute soda solution, evaporated, strongly acidified with acetic acid, and saturated with sodium chloride. The filtrate is precipitated with phosphotungstic acid, the precipitate washed with hot water acidified with sulphuric acid, and warmed with baryta-water. The liquid is decanted, freed from the excess of baryta, treated with lead hydroxide in the cold, the excess of lead removed by dilute sulphuric acid, a few crystals of salicylic acid added, and the product submitted to dialysis until the amount of ash does not appreciably diminish. It is then filtered, concentrated to a syrup and poured into 96 per cent. alcohol. The precipitate resembles in every respect that obtained from a fibrin peptone solution. It is tough, dissolves gradually in cold, readily in hot water; the dried pulverulent substance has a yellowish colour, dissolves in almost all proportions in water, more sparingly in dilute spirit, and is insoluble in 85 per cent. alcohol; it is free from albuminoïds and from hemialbumose, its aqueous solution giving no precipitate with acetic acid and potassium ferrocyanide, nor with lead acetate, no reaction with ferric acetate, no precipitate with sodium chloride (or sodium chloride and acetic acid), none with dilute nitric acid, and no reaction with sodium sulphate and acetic acid (contrary to Griessmayer's statement). Its solution gives, however, the characteristic biuret reaction with alkali and copper sulphate.

A series of experiments is described, showing that peptone is not only not precipitated by cupric hydroxide, but that its solution, even when considerably diluted, is capable of dissolving the latter.

The following is the composition of peptone: Ash, 1.7883 per cent., C = 53.62 per cent., H = 7.15 per cent., and N = 17.01 and 16.76 per cent., the percentage of the elements being calculated on ash-free substance. Its specific rotary power is  $[\alpha]_D = -52.79^\circ$ .

A. K. M.

**Nuclein of Grape Stones.** By C. AMTHOR (*Zeit. Physiol. Chem.*, 9, 138—144).—The nuclein was separated by digesting the pounded stones from the ripe fruit, with a 0.5 per cent. solution of sodium hydroxide, filtering, and allowing the filtrate to flow into dilute hydrochloric acid. After purification, the determination of phosphorus and sulphur in the dry substance gave P = 0.89 per cent., S = 0.35 per cent. Heated with water in a sealed tube it underwent decomposition, 90 per cent. of the phosphorus being split off in the form of soluble compounds. The solution gave with ammonia a deep red-violet coloration. The author has also studied the changes which occur during ripening in the proportions of various constituents containing phosphorus, namely: (1) lecithin (soluble in alcohol ether), (2) phosphates (extracted by hydrochloric acid from residue from former), and (3) nuclein (phosphorus determined in residue). The following proportional numbers, representing ratios of P per cent., were obtained at three successive stages, viz.:—

	(1.)	(2.)	(3.)
6th September .....	1	: 9.4	: 1.1
30th       "       .....	1	: 10.0	: 0.9
30th October .....	1	: 9.4	: 0.8

C. F. C.

**Albumin and its Oxidation.** By O. LOEW (*J. pr. Chem.* [2], 31, 129—154).—From the study of the silver compounds of albumin, the author shows that the formula  $C_{72}H_{112}N_{18}SO_{22}$ , assigned to it by Lieberkühn, must be trebled. The origin of the numerous substances obtained from albumin the author believes to be due—not to their pre-existence in that substance, but to the mobility of its atoms. That the oxygen is probably mostly present as hydroxyl, and not in the form of ketone- or aldehyde-groups is shown by the fact that when albumin is treated for weeks at the ordinary temperature with alkaline or acid hydroxylamine solutions, no change occurs, but prolonged heating causes reduction, whilst substances of peculiar properties are obtained. Albumin when boiled with caustic potash evolves one-ninth of its nitrogen as ammonia, whilst when treated under pressure at  $150^\circ$  with baryta, one-fifth of the nitrogen is eliminated as ammonia. This elimination of the nitrogen does not necessarily show that it is loosely combined, for many substances are known containing several amido-groups, which, on heating, lose ammonia with formation of imido-groups. Albumin is not affected by nascent hydrogen, but with bromine it forms an additive product. 100 grams of albumin, treated for several weeks in the cold with 50 c.c. of bromine, gradually changed to a half-fluid mass, which, even after washing with water,

remained yellow, owing to loosely combined bromine. Analysis gave 24.02 per cent. of bromine. Continued washing with water causes gradual decomposition, but treatment with zinc and hydrochloric acid, or with sodium sulphide, removes the yellow colour, and the white product obtained contains 16.16 per cent. of bromine. This amount is equal to 4 atoms of bromine combining with 1 molecule of albumin on Lieberkühn's formula. The yellow bromide dissolves in ammonia with evolution of nitrogen; on addition of acids to this solution, a white precipitate containing 13.10 per cent. of bromine is obtained. That leucine does not pre-exist in albumin, is shown by the behaviour of the latter with osmic acid and potassium permanganate. Dilute solutions of albumin and potassium permanganate yield benzoic and acetic acids. The end products of the oxidation of albumin with permanganate are benzoic, acetic, oxalic, succinic, formic, and hydrocyanic acids, ammonia and carbonic anhydride. Between albumin and these final products, a number of syrupy nitrogenous substances of acid character were obtained, which under the influence of strong bases or acids chiefly yield amidovaleric acid. H. P. W.

**Oxidation of Albumin with Potassium Permanganate.** By R. MALY (*Monatsh. Chem.*, **6**, 107—156).—The only product formed in considerable quantity by the moderated oxidation of the albuminoids is an uncrystallisable acid containing sulphur and nitrogen, described by Brücke (*Monatsh. Chem.*, **2**, 23). This acid is only formed by the oxidation of the unpeptonised albuminoids, potassium permanganate equal to 50 per cent. of the dry albuminoid employed being required to destroy all the latter; 50—100 per cent. of permanganate produces a speedy oxidation, a large yield of Brücke's acid, and also of another acid not precipitated by mineral acids; a still larger amount of permanganate destroys Brücke's insoluble acid, and converts it into another substance, also not precipitated by acids.

Brücke's acid, or *oxyprotosulphonic acid*, leaves no ash on burning, is practically insoluble in water, and dissolves in concentrated mineral acids from which it is precipitated unaltered by addition of water. When dissolved in the minimum amount of an alkali, an acid solution is obtained, due in all probability to the formation of an acid salt; its acid properties are also shown by its solubility in, and decomposition of, sodium acetate, phosphate, &c.

The acid is undoubtedly homogeneous; it differs from albumin by containing a larger amount of oxygen, as shown by the comparison of its composition with that of albumin:

	C.	H.	N.	S.	O.
Oxyprotosulphonic acid.	51.21	6.89	14.59	1.77	25.54
Albumin.....	52.98	7.09	15.70	1.82	22.41

about 4 atoms of oxygen being added for each atom of sulphur present. It would seem that the sulphur is oxidised to the sulphonic group, as, unlike albumin, the acid does not yield lead sulphide when treated with lead acetate, and gives sulphites when fused with caustic soda or heated under pressure with baryta-water.

The salts are not crystalline, those of the alkalis and alkaline earths are soluble in water; the barium, copper, and sodium salts contain equivalent amounts of metal, namely, 11.73, 5.46, and 4.08 respectively. The free acid suspended in acidified water is digested by pepsin. Heated with baryta at  $170^{\circ}$  for five days, it gives the same products of decomposition, with the exception of tyrosine, as are yielded by albumin, namely, carbonic, acetic, and oxalic acids, ammonia, pyrroline, and leucine. Albumin, when fused with caustic soda yields parahydroxybenzoic acid, oxyprotosulphonic acid does not. By the putrefaction of albumin, but not of oxyprotosulphonic acid, aromatic compounds, phenol and indole, &c., are formed. The presence of these aromatic groups in oxyprotosulphonic acid are, further, not indicated by Millon's reagent, and hence they may have suffered hydroxylation, still no trace of di- or tri-oxybenzene compounds could be obtained. That the aromatic group still exists in oxyprotosulphonic acid is shown by fusing with alkali, when benzene is liberated, and by boiling with excess of permanganate when benzoic acid is formed, but no phthalic acids; albumin also yields benzoic acid.

The soluble acid formed at the same time as the oxyprotosulphonic acid can be isolated by phosphotungstic acid or by lead acetate. By fractionation of the barium and sodium salts, containing 12.1 per cent. barium and 4.1 per cent. sodium, it is shown that the acid is homogeneous; its composition—C 48.20; H 6.65; N 13.40; S 2.00; O 30.00—and reactions show it to be an albuminoid and a sulphonic acid, and to have lost some of the fatty groups by oxidation.

The acid formed by the oxidation of oxyprotosulphonic acid with excess of permanganate at ordinary temperatures is isolated by means of its lead and barium salts; the last contains about 28.2 per cent. barium. The acid contains nitrogen and sulphur and gives the biuret reaction.

H. B.

**New Reaction of Carbonic Oxide Hæmoglobin.** By S. ZALESKI (*Zeit. physiol. Chem.*, 9, 225—228).—A few drops of a dilute solution of cuprous chloride added to 5—10 c.c. of blood, containing carbonic oxide, occasions the separation of a bright red flocculent substance; normal blood similarly treated gives a dark brown precipitate. Similar results are obtained with solutions of the cupric salts. The reaction was obtained with blood which had been treated with carbonic oxide, and allowed to stand 12 days at the ordinary temperature. No such reaction was obtained with blood treated with other gases.

C. F. C.

**Colouring Matter of the Blood.** By M. NENCKI and N. SIEBER (*Ber.*, 18, 392—399).—When the compound  $(C_{32}H_{31}ClN_4FeO_3)_4, C_5H_{12}O$  (this vol., p. 70) is heated at  $130$ — $135^{\circ}$ , it loses amyl alcohol alone, and hæmin crystals,  $C_{32}H_{31}ClN_4FeO_3$ , remain. On dissolving the product in dilute soda solution and adding hydrochloric acid, hæmatin,  $C_{32}H_{32}N_4FeO_4$ , is precipitated; this probably contains hydroxyl in the place of the chlorine of the hæmin. When hæmin and hæmatin are boiled for some time with acetic anhydride, a change in composition is effected, probably from the introduction of acetyl-groups.

Hæmin also appears to yield an additive compound with acetic anhydride. No hydrochloric acid is given off, and this fact supports the assumption that the chlorine is united to carbon or iron, and is not present as hydrochloric acid.

Assuming that it might be an additive compound of hæmin with albumin,  $C_{32}H_{31}ClN_4FeO_3 + C_{604}H_{604}N_{160}S_3O_{186}$ , the authors prepared hæmoglobin from horse-blood according to the usual method, but found it to be absolutely free from chlorine and also from phosphorus. Concentrated nitric acid acts very violently on dry hæmoglobin with production of *paranitrobenzoic acid*; globulin and some other albuminoids also yield the same product. With the view to coagulate hæmoglobin, the purified substance was treated with 93 per cent. alcohol for 16 hours at about  $8^\circ$ ; the product was found, however, to consist of homogeneous rhombic prisms of the colour of hæmoglobin, and insoluble not only in alcohol and ether, but also absolutely insoluble in water. This so-called *parahæmoglobin* is either an isomeride or polymeride, its percentage composition being practically identical with that of hæmoglobin. Dried over sulphuric acid, it loses 1.88 per cent. at  $115-120^\circ$ . It dissolves in dilute solutions of the fixed alkalis, and on adding an acid a brown amorphous precipitate is produced. Parahæmoglobin is slowly acted on by dilute aqueous mineral acids, and may be boiled for a long time with acidulated alcohol without decomposition, so that it is not suitable for the preparation of hæmin.

A. K. M.

**Decomposition-products of the Colouring Matters of the Blood.** By F. HOPPE-SEYLER (*Ber.*, 18, 601—606).—The author discusses the relative merits of his own and Nencki and Sieber's (this vol., p. 69) processes, for the preparation of crystalline hæmin. The author admits that the extraction with amyl alcohol acidified with hydrochloric acid is more rapid than that with glacial acetic acid, but points out that even pure amyl alcohol acidified with hydrochloric acid becomes coloured by comparatively short digestion, and this coloration is imparted to the hæmin crystals. He considers the use of glacial acetic acid to be preferable to that of amyl alcohol. He also discusses the results obtained by Nencki and Sieber (*loc. cit.*), and comes to the conclusion that these results do not justify the formula and equations proposed by those investigators.

L. T. T.

**Conchiolin, and the Occurrence of Chitin in the Cephalopoda.** By C. F. W. KRUKENBERG (*Ber.*, 18, 989—993).—Conchiolin may be obtained in exceptional purity from the egg-shells of certain molluscs (*Murex trunculus*, *Buccinum undatum*). These are treated with cold dilute hydrochloric acid, extracted with alcohol and ether to remove the fat, and freed from albuminoids by acid pepsin and neutral trypsin solutions at  $38^\circ$ . The mucin is then removed by 3—4 days' maceration with 10 to 20 per cent. soda solution, when pure conchiolin remains. In its properties and composition it appears to be closely related to cornein. Both compounds are soluble in water, alcohol, ether, cold and boiling acetic acid, insoluble in dilute mineral acids, and are acted on by soda with difficulty, which colours them yellow (distinction from chitin). On boiling conchiolin with dilute sulphuric acid,

leucine is produced (not cornicrystallin, distinction from cornein), and also tyrosine, glycine, and a substance which reduces alkaline copper sulphate. Leucine also appears to be the chief product when conchiolin is evaporated with concentrated hydrochloric acid. Conchiolin gives none of the colour reactions which characterise the albuminoids; it yields no red coloration with Millon's reagent (distinction from cornein), is coloured only yellow by the xanthoprotein reaction, does not colour boiling concentrated hydrochloric acid either red, purple, or bluish-violet, neither does it give Adamkiewicz's reaction. Its composition corresponds with the formula  $C_{30}H_{48}N_9O_{11}$ , so that it bears the same relation to cornein,  $C_{30}H_{44}N_9O_{13}$ , as ethylene alcohol does to oxalic acid.

A substance of very different composition is obtained from *Loligo vulgaris* and from *Sepia officinalis*. Its behaviour on boiling with dilute sulphuric acid and on treatment with alkali, indicates its identity with chitin, and like this it yields glucosamine hydrochloride on evaporation with concentrated hydrochloric acid. Its identity with chitin is further confirmed by analysis. The occurrence of chitin in molluscs has often been stated, though not previously proved.

A. K. M.

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## Physiological Chemistry.

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**Different Degrees of Resistance in Protoplasm.** By O. LOEW (*Pflüger's Archiv*, 35, 509—516).—Living protoplasm in different organisms differs very much in its behaviour with various reagents, such as silver solutions, ammonium chloride, alkaloids, &c.

A. J. G.

**Influence of Salts on certain Digestive Processes.** By E. PFEIFFER (*Chem. Centr.*, 1885, 26).—Sodium chloride accelerates the conversion of starch into sugar by means of salivary and pancreatic extract. A sample of starch solution which has been treated with sodium chloride will be free from starch in one-third or one-fourth the time required by a similarly concentrated and treated solution to which no sodium chloride has been added. The rapidity of the process of saccharification increases directly with the quantity of sodium chloride added. Sodium carbonate hinders this change to a considerable extent, and in large quantities appears to prevent it altogether. Sodium and magnesium sulphates also produce a similar effect, the latter, however, in a less marked degree.

The diffusion of peptone solutions through parchment is assisted by the addition of  $\frac{1}{2}$  to 1 per cent. of sodium chloride or sulphate, and especially so by the former salt.

J. K. C.

**Nitrogenous Substances Insoluble in Gastric Juice.** By A. STUTZER (*Zeit. physiol. Chem.*, 9, 211—221).—In almost all vegetables there are found three groups of nitrogenous substances: one,

soluble in water, and represented by asparagine; the second, comprising albumin, dissolved by the hydrochloric acid pepsin of the stomach, and chemically distinguished from amides by forming *insoluble* compounds with copper hydroxide in neutral solutions; the third group is composed of all those nitrogenous substances which are not soluble in water or in acid pepsin. The author undertook the examination of the latter group, and as the results of experiments on the living animal would probably be rendered doubtful by the presence of mucin and other nitrogenous matters in the excreta, due to the transformation of tissue, he decided on employing artificial digestion. The substance used for preliminary experiments, was commercial cocoa-nut cake, largely used as cattle fodder. This was treated with acid pepsin solution, and afterwards with variously prepared extracts, of pancreas, in order to remove the nitrogen as much as possible. The results showed that the alkaline pancreatic extract had less effect on protein matters than the acid pepsin, although in some cases the results were very close. The examination of other animal secretions suggested itself to the author. Hoppe-Seyler denies the power of intestinal secretions to dissolve albumin, and even should it be proved hereafter that there are ferments in the organism which have the power of digesting albumin, it must be remembered that such ferments have a less powerful action than either the gastric or pancreatic juices, and that food materials which are unaffected by these two secretions are probably valueless as nourishment.

To prepare the extract of pancreas, the author took the pancreas of an ox (400 grams), freed as much as possible from fat, exposed it freely to the air for 24 hours, rubbed it down finely with sand, covered it with dilute glycerol (1 litre glycerol and 1 litre water), and after 4—6 days pressed and filtered. When used, this extract must always be made alkaline by the addition of soda.

Some of the experiments were made to determine if soda alone was able to dissolve nitrogenous compounds. Two samples of finely ground barley straw were digested with artificial gastric juice, after which there remained in the undissolved portion a mean of 0.206 per cent. nitrogen. After further digestion with  $\frac{1}{2}$  per cent. soda solution at 40° for several hours there remained nitrogen undissolved 0.105 per cent. Experiments with leaves of grass and palm-nut kernels yielded similar results. Whether the soda acts simply as a solvent or causes a true decomposition of the substances acted on, is a question the author cannot answer.

A quantity of palm-nut cake was first treated with freshly prepared acid pepsin solution, after which it contained an average of 0.461 per cent. nitrogen. Portions were then treated with 100 c.c. of pancreas extract to 2 grams of residue (a proportion preserved in all the experiments),  $\frac{1}{2}$  and 1 per cent. soda solutions being used to give an alkaline reaction. The results were negative, the differences being within the limits of experimental error. Other observations convince the author that  $\frac{1}{2}$  to 1 per cent. soda solution without any ferment act as solvents equally well as when pancreas ferment is present; this he explains by the organic matter from the pancreatic glands diluting the soda and gradually diminishing its solvent powers.

A mixture of lucerne and grass hay which left a residue after digestion of 0.293 per cent. nitrogen, after treatment with pancreas solution containing 1 per cent. soda, left 0.213 per cent.; with  $\frac{1}{2}$  per cent. soda, 0.271 per cent. In the former case 27 per cent., in the latter but 7 per cent. of the difficultly soluble nitrogen was dissolved. Similar experiments with the following substances show the percentages dissolved by the pancreas solutions:—

Cocoa powder, 26 per cent.; dry flesh meal, 24 per cent.; ship's biscuits, 27 per cent. J. F.

**Absorption, Formation, and Storage of Fat in Animals.** By J. MUNK (*Bied. Centr.*, 1885, 165—166).—Rape-seed oil given to a dog was stored up to a considerable extent, and the fat of the dog was afterwards found to consist of 82.4 per cent. of oleic and 12.5 per cent. of solid fatty acid, whilst the ordinary dog fat consists of 65.8 per cent. oleic, and 28.8 per cent. of solid fatty acid; moreover, erucic acid was obtained from the fat, proving the presence of the rape oil. In addition to experiments described previously (*Abstr.*, 1884, 852), the author has shown that in the case of the dog, the fatty acids of mutton suet are capable of exercising the same influence on the albuminous decomposition as mutton suet or lard. After feeding with flesh and the acids of mutton suet, the fat in the dog consisted of 3 parts mutton suet and 1 part true dog fat. E. W. P.

**Amount of Sugar and Reducing Substances in the Blood under Various Circumstances.** By J. G. OTTO (*Pflüger's Archiv*, 35, 467—498).—The following are some of the conclusions arrived at by the author:—Normal blood contains another reducing and fermentable substance besides sugar. Arterial blood is somewhat richer in sugar than venous blood; the total reducing substance contained in both is, however, identical. In hypnotism produced by morphine, chloral, or chloroform, the amount of reducing substance in the blood is considerably increased. There is no marked difference in the amount of sugar in the blood of a newly-born infant and that of its mother. During inanition, if not too long continued, the total amount of sugar is essentially unaltered, but the venous blood is either richer, or at least as rich in sugar as the arterial blood.

A. J. G.

**Pancreatic Function of the Cephalopod Liver.** By A. B. GRIFFITHS (*Chem. News*, 51, 160).—In addition to the facts already brought forward (*Abstr.*, 1884, 94) to show that the cephalopod liver is pancreatic in function, the following are now adduced. Portions of the organ removed from a fresh sepia had an alkaline reaction, converted starch into dextrose, and oil into fatty acids; 6 mgrms. of the tissue of the organ rendered 15 c.c. of milk transparent in four hours. Moreover, the ferment, removed from the organ, previously hardened by treatment with alcohol, by extraction with glycerol, and subsequent precipitation with alcohol, converted starch into dextrose, and fibrin into leucine and tyrosine. The organ

contains neither glycocholic nor taurocholic acid nor glycogen; it is therefore evident that this so-called "liver" is a true pancreas.

D. A. L.

**Excretion of Carbamide in the Human Subject.** By C. GENTH (*Pflüger's Archiv*, **35**, 581—597).

**$\beta$ -Hydroxybutyric Acid in Diabetic Urine.** By A. DEICHMÜLLER, F. SZYMANSKI, and B. TOLLENS (*Annalen*, **228**, 92—95).—The authors confirm the results of Külz (*Zeitschr. f. Biologie*, **20**, 165) Min-kowski (*Archiv f. exp. Pathol and Pharmacol*, **18**, 35 and 147), and other investigators, who have detected the presence of  $\beta$ -hydroxybutyric acid in the urine of patients suffering from diabetes.

W. C. W.

**Cystine not Present in Normal Human Urine.** By STADTHAGEN (*Zeit. physiol. Chem.*, **9**, 129—137).—The author's experiments were made to ascertain whether cystine was a normal or abnormal constituent of human urine. It is known that in addition to ordinary sulphates, urine contains a considerable number of combinations of sulphur with organic bodies. Salkowski estimates the proportion of such combinations as containing fully one-fifth of the total sulphur, but the author thinks that proportion too high. Munk and Gscheidlen have estimated the compounds of cyanogen with sulphur, and Salkowski has isolated from normal urine small quantities of an acid containing both sulphur and nitrogen; but the quantity of sulphur contained in these substances still leaves the greater part of the sulphur existing in organic combinations unaccounted for. The richness of cystine in sulphur seems to indicate that the missing quantity exists in this form. Other authors, Salkowski, Mauthner, and Haas for example, have held the same opinion. The latter observed the lævorotatory power of normal urine, and attributed it to the presence of cystine, which is strongly lævorotatory. On the other hand, Külz directly denies its presence in normal urine, and its very slight solubility in that fluid has caused it to be sought for in the sediment; but it is quite possible that more soluble modifications of it may exist.

The author has examined numerous residues from normal urines with many reagents, and extracts with various menstrua, but from none of them has he been able to obtain positive indications of the presence of cystine; he also sought a sulphur acid which might bear the same relation to cystine as Jaffe and Baumann's phenylmercapturic acid to phenylcystein, but equally without success. The author describes other experiments, but concludes with the opinion that cystine is not present in normal human urine, and that the lævorotatory substance of Haas is not a modification of it.

J. F.

**Poisonous Action of Hydroxylamine.** By O. LOEW (*Pflüger's Archiv*, **35**, 516—527).—Hydroxylamine is a most active poison for the lower organisms, both animal and vegetable, and is distinguished from most other substances by the very wide range of its toxic powers. It is therefore a powerful antiseptic, rapidly killing fungi, diatoms,

infusoria, &c. Seeds of the sunflower, maize, buckwheat, clover, &c., did not germinate after immersion in solutions of hydroxylamine hydrochloride (1 per 1000). The author considers that the poisonous nature of hydroxylamine and of phenylhydrazine points to the occurrence of one or more aldehyde groups in protoplasm. A. J. G.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Metastasis in Leaves.** By T. SACHS (*Chem. Centr.*, 1884, 945—947).—The author has investigated the formation and disappearance of starch in the chlorophyll granules of leaves under different conditions. The experiments were made in the summer of 1883, with 18 dicotyledenous plants, belonging to various families. The presence of starch in the green leaves is detected by the following process:—The fresh green leaves are boiled with water for 10 minutes, and then immersed in 96 per cent. alcohol. After this treatment the leaves are placed in a strong solution of iodine, made by dissolving iodine in alcohol, and then diluting with distilled water until the liquid has a dark brown colour. They are allowed to remain in this liquid for about an hour, or until they no longer acquire colour. If after this the leaves are stained dark yellow, the chlorophyll granules contained no starch; if they are stained slightly black very little starch is present; and if dead black or black with a metallic lustre, large quantities of starch are present, the maximum quantity being indicated by a distinct metallic lustre. By this means it is shown that starch disappears from the chlorophyll granules when the plants are allowed to grow for a long time in a dark place, and in the light from those portions of the leaf which have been covered by paper or tin-foil. The leaves of many plants are found at sunrise to contain no starch, but by the evening large quantities are formed, which again disappears during the night. Generally a warm atmosphere facilitates the process, whilst a low temperature has the reverse effect. The conditions of growth have much to do with these changes. Tobacco when grown freely in soil exhibits them, but when grown in a flower-pot shows no variation in the starch contents. It appears that during the night the starch is dissolved, and passes into the stem. The disappearance of the starch is probably due to its conversion into sugar by means of a soluble ferment. Up to the present time all physiological observations with green leaves have been in relation to surface area, and not to weight; the author therefore estimates the quantity of starch which is developed or changed in a square metre of leaf surface in a unit of time. This is done by drying and weighing measured pieces of the leaf, as free as possible from nerves and ribs, both in the morning and evening. In this way it was found that during each hour of the day a square metre of the leaf of *Helianthus* gained 0.914 gram, of *Cucurbita* 0.680 gram, and of *Rheum*

0.652 gram of starch. During each hour of the night *Helianthus* leaves lost 0.974 gram, and *Cucurbita* 0.828 gram of starch. By adding these two results together the total assimilation of material by the leaf is obtained. Calculating from these data it appears that under the conditions described, which are those of an average summer's day of 15 hours, one square metre of the leaf of *Helianthus* and *Cucurbita* gains 24 grams of starch, while the total assimilation in the case of *Helianthus* is 36 grams, and in that of *Cucurbita* 185 grams.

W. R. D.

**Respiration of Plants.** By H. MÖLLER (*Ann. Agronom.*, **11**, 140—141; from *Ber. deutsch. bot. Gesells.*, 1884, **2**, 35—41 and 306—321).—The author concludes from his experiments with purified nitrous oxide that plants cannot decompose this gas by assimilating its oxygen. An atmosphere of nitrous oxide arrests the geotropism and growth, prevents germination but does not destroy the germinative power, and stops the circulatory movements of the protoplasm, thus behaving throughout like an indifferent gas.

The intramolecular respiration of certain plants and seeds in an atmosphere of nitrous oxide has also been studied. The author agrees with Pfeffer that in the case of most of the oily and starchy seeds the carbonic anhydride evolved by intramolecular respiration is about one-third of that evolved during normal respiration. In the case of some plants, however, the intramolecular respiration is much greater.

J. M. H. M.

**Large and Small Hulled Beetroot Seed.** By F. KUDELKA and M. HOLLRUNG (*Bied. Centr.*, 1885, 184—186).—The tables of results show the energy of germination possessed by the seeds in larger hulls is greater, and the small plants are stronger than those produced from the seeds of the small hulls. The ratio existing between the number of plants from small and from large hulls is 1 : 1.71, and the ratio between the weights of the plants is 1 : 2.2. Consequently as the larger hulls are more energetic, the plants produced have greater opportunity to resist attacks of insects and to produce larger roots. Hollrung, on the other hand, finds the difference between the energy of germination of small and large hulls, is in favour of small hulls; he also is unable to find that the plants from large hulls are any stronger than those from the small.

E. W. P.

**Existence of Manganese in Plants.** By G. CAMPANI (*Gazzetta*, **14**, 515—516).—This paper is a controversial note, and contains no new chemical facts.

V. H. V.

**Percentage of Alkaloids in Different Varieties of Lupines.** By E. HILLER (*Landw. Versuchs-Stat.*, **31**, 336—341).—The results which Hiller has obtained regarding the percentage of total alkaloids in varieties of lupines are lower by 0.04—0.15 per cent. than those obtained by Tauber. *L. hirsutus* is, however, an exception, as 0.02 per cent. higher was found. Variation in the percentage due to weather, manure, and soil was also found. On examining the unripe seeds for alkaloids, it appeared that in the case of *L. luteus* the per-

centage was the same; in *L. hirsutus*, slightly less; and in *L. termis*, slightly more. Tables showing the percentage of solid and liquid alkaloids present in all varieties are given. E. W. P.

**Adonis Cupaniana.** By V. CERUELLO (*Gazzetta*, 14, 493—495).—In this paper an account is given of the *Adonis cupaniana*, a species of the *Ranunculaceæ*, flowering in spring. From various parts of the plant an essential principle, adoninidine, can be extracted. When injected into a frog, it produces irregularity of the auricular systole, and finally death; but in mammals, irregularity of the ventricular systole. It is proposed to use this substance, like digitaline, as an antiscorbutic. V. H. V.

**Feeding Milch Cows with Ensiled Sugar-beet Sections.** By M. SCHRODT and H. HANSEN (*Bied. Centr.*, 1885, 166—169).—The cows were fed with ensiled beet sections in addition to ordinary feeding, consisting of chaff, bran, and cotton cake; but during the periods when the sections were given, ordinary roots were omitted, and *vice versa*. Taking into account all the conditions of the experiments, and making allowances for the variations due to lactation, the authors come to the conclusion that the sections have had no advantageous influence either on the quantity or the quality of the milk. E. W. P.

**Cultivation of Sorghum Saccharatum.** By E. v. SZECHENYI, junr. (*Bied. Centr.*, 1885, 186—188).—A short account of an attempt to grow sorghum in Hungary. The syrup obtained (at 42° B.) contained 52.1 saccharose and 28.62 invert sugar with 15.74 water. The composition of the seeds closely resembled that of barley. Altogether the results were satisfactory. E. W. P.

**Cultivation and Preservation of certain Cereals.** By STREBEL and others (*Bied. Centr.*, 1885, 189—197).

**Manuring Potatoes with Potash Salts.** By BOURSIER and ST. ANDRÉ (*Ann. Agronom.*, 11, 143).—Six varieties of potatoes were grown with different manures in a soil containing 0.083 per cent.  $P_2O_5$ , 0.202 per cent.  $K_2O$ , and 0.110 per cent. N. The mean results obtained with the various manures were—

Superphosphate of lime....	20,242	kilos.	per hectare.
Farmyard manure .....	19,207	„	„
Superphosphate and sodium nitrate .....	19,191	„	„
Superphosphate, sodium nitrate, and potassium chloride .....	18,583	„	„
Superphosphate and potassium nitrate.....	18,076	„	„

There appear to have been no unmanured plots. The authors conclude that the potash salts exerted no influence.

J. M. H. M.



**Farmyard Manure.** By A. AUDOYNAUD and E. ZACHAREWICZ (*Ann. Agronom.*, 11, 129—137).—From the authors' analyses, compared with those of Boussingault and others, it appears that the nitrogen and potash contained in cows' urine do not vary very greatly in amount, and that for the purpose of general calculations as to the composition of farmyard manure, it may be taken that a cow contributes 10·5 grams nitrogen and 13·6 grams potash per litre of urine, equal to 31·5 kilos. nitrogen, and 40·8 kilos. potash per annum. Only a portion of the potash is present as bicarbonate; the remainder exists as sulphate and hippurate. J. M. H. M.

**Employment of Cider Mark as Manure and Fodder.** By G. LECHARTIER (*Bied. Centr.*, 1885, 163—165).—The apple pulp not having been washed, but merely pressed, consists of water and volatile matter 75·75 per cent., albuminoids 1·37, fat 1·26, sugar 3·17, carbohydrates 5·01, fibre 12·08, ash 0·65. This pulp must not contain any rotten apples, which induce the butyric fermentation and render it unpalatable to cattle. As a manure it is worth 5 francs per 1000 kilos., and it contains per cent. N 2·02, CaO 0·59—0·61, MgO 0·41—0·87, K<sub>2</sub>O 2·08—3·65, P<sub>2</sub>O<sub>5</sub> 0·70—0·84. E. W. P.

**Black Soil from Manitoba.** By J. M. H. MUNRO (*Chem. News*, 51, 159—160).—The sample is from the first 12 inches of black prairie soil from the neighbourhood of Birtle, Manitoba. It contained 6·70 per cent. of moisture, and when dried at 100° consisted of 9·70 organic matter and water, 1·41 small stones and gravel, 2·45 gravelly sand, 64·20 coarse sand, 11·70 fine sand, and 10·54 burnt clay. The fine earth, which passed through a sieve 30 meshes to the inch, dried at 100°, was composed of 10·07 per cent. organic matter and combined water, 83·41 silica and insoluble silicates, and Fe<sub>2</sub>O<sub>3</sub>.Al<sub>2</sub>O<sub>3</sub> 4·195, CaCO<sub>3</sub> 0·96, MgO 0·487, K<sub>2</sub>O 0·271, P<sub>2</sub>O<sub>5</sub> 0·195, Cl 0·010, SO<sub>3</sub> trace = 99·598 total, total nitrogen = 0·412, minerals soluble in water = 0·048, K<sub>2</sub>O soluble in water = 0·0081. It is a sandy soil, contains much vegetable matter, a very high proportion of nitrogen and magnesia, abundance of potash and phosphoric acid, but is rather poor in lime. D. A. L.

**Improvement of Sheep Manure by Kainite.** By A. RITTER (*Bied. Centr.*, 1885, 210).—Kainite may be added with advantage to sheep dung, as it prevents the formation of mould; it is preferable to gypsum, as moisture is retained. E. W. P.

**Composition of Wood Ashes.** By WAGNER (*Bied. Centr.*, 1885, 210).—The percentages of phosphoric acid and potash in eight samples of wood ashes are here given, but the class of wood is not stated. Phosphoric acid varies from 0·81—4·31 per cent., and potash 2·03—7·9 per cent. E. W. P.

## Analytical Chemistry.

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**Analytical Operations and Apparatus.** Part II. By R. WOLLNY (*Zeit. anal. Chem.*, **24**, 202—216; compare Abstr., 1885, 591).

**Use of Lime-water in Zinc Gasometers.** By J. LÖWE (*Zeit. anal. Chem.*, **24**, 221).

**Bottles for Reagents.** By A. GAWALOVSKI (*Zeit. anal. Chem.*, **24**, 216—218).

**Burette for Solutions which are easily Reduced and which Attack India-rubber.** By A. GAWALOVSKI (*Zeit. anal. Chem.*, **24**, 218).

**New Form of Apparatus for Continuous Percolation with Boiling Liquids.** By J. C. THRESH (*Pharm. J. Trans.* [3], **15**, 281).

**Phenolphthaleïn as an Indicator.** By J. H. LONG (*Chem. News*, **51**, 160—163).

**Quantitative Spectrum Analysis.** By G. KRÜSS (*Ber.*, **18**, 983—986).—In the quantitative examination of solutions by means of the spectroscope, the concentration is ascertained by determining the coefficient of absorption. To do this, the observing telescope is provided with an adjustable slit, by means of which a narrow strip of nearly homogeneous light may be cut off from the rest of the spectrum and examined separately. The author has made experiments to determine the limit to which the slit in the eye-piece may be narrowed without diminishing the accuracy of the determination. He finds this limit to be 0.263 mm. in his instrument. The magnifying power of his eye-piece is 13.4, so that a spectral region 3.524 mm. wide is seen. The value  $\frac{3.524}{V} = C$  ( $V$  being the magnifying power of the ocular) is therefore proposed as the constant breadth to be recommended for the slit in the eye-piece. A. K. M.

**Estimation of Chlorides in Urine.** By C. ARNOLD (*Pflüger's Archiv*, **35**, 541—557).—The author has investigated Volhard's method (Abstr., 1878, 746), and confirmed the accuracy of the results obtained in the analysis of a large number of normal and pathological urines, by comparison with those obtained by determining the chlorine in the ash of the urines. The method recommended is as follows:—10 c.c. of urine is mixed with 10—20 drops of nitric acid of sp. gr. 1.185, 2 c.c. of a solution of ammonium alum, and 10—15 drops of potassium permanganate solution, and the liquid then titrated according to Volhard's directions (*loc. cit.*). A. J. G.

**Vortmann's Method for Estimating Chlorine in the Presence of Bromine.** By E. BERGLUND (*Zeit. anal. Chem.*, **24**, 196—199).—It is not easy to remove all the bromine even by repeated evaporation with acetic acid (2—3 per cent. strength) and lead dioxide. If the acetic acid is stronger than 5 per cent., some of the chlorine is also liberated. Somewhat better results are obtained by adding a sulphate to the solution, so as to hinder the formation of lead bromide, which is decomposed with difficulty, but even then this method is not very satisfactory. S. R.

**Quantitative Separation of Chlorine and Bromine.** By E. BERGLUND (*Zeit. anal. Chem.*, **24**, 184—195).—A mixture of hydrogen potassium sulphate and potassium permanganate when added to a solution of a bromide, liberates all the bromine, whilst in the cold it has no action on a chloride. The free bromine can be easily and completely removed by passing a current of air through the solution. The bromine is absorbed by weak aqueous soda. The presence of potassium nitrate in the solution does not interfere with the separation. S. R.

**New Reagent for the Absorption of Oxygen.** By O. V. D. PFORDTEN (*Annalen*, **228**, 112—126).—The last traces of oxygen can be removed from a gas by a solution of chromous chloride. Chromous acetate prepared by Moissan's process (*Ann. Chim. Phys.* [5], **25**, 416) is brought into a couple of flasks from which the air has been expelled. These flasks are connected together in the usual way with glass tubes, and in addition each flask is provided with a tap funnel filled with dilute hydrochloric acid. A small quantity of acid is admitted by the tap funnels into each of the flasks, converting a portion of the chromous acetate into chloride. The solution of the chloride has a blue colour, which is rapidly turned green by oxygen. This change in colour may be used as a qualitative test for traces of oxygen. W. C. W.

**Use of Sulphuric Acid to Oxidise Sulphides for the Estimation of their Metals.** By E. DIVERS and T. SHIMIDZU (*Chem. News*, **51**, 193).—When nitric acid is used for the oxidation of sulphides, as is well known, the action is sometimes very violent; it is always accompanied by disagreeable fumes, the separation of sulphur, and frequently by loss; moreover, when the action has ceased the excess of nitric acid has to be got rid of and the various metals reduced. The use of sulphuric acid in place of nitric acid is attended by none of these disadvantages, the finely powdered sulphide may be mixed with all the concentrated acid required, gentle heat can be applied at once and kept up so as to maintain a gentle effervescence, there is no inconvenient separation of sulphur or evolution of fumes, and, finally, the product is ready for immediate treatment.

Boiling hot strong sulphuric acid oxidises ferrous to ferric sulphate, therefore ferric sulphate only is obtained by treating pyrites with hot concentrated sulphuric acid. In a similar manner mercuric sulphide is not attacked by cold acid, but by the boiling acid, is converted largely into mercuric sulphate, but to a certain extent into *sulphato-sulphide*,

probably  $\text{HgSO}_4 \cdot 2\text{HgS}$ , which yields some black mercury sulphide when treated with potassium hydroxide solution, but seems to be decomposable by the continued action of sulphuric acid. D. A. L.

**Estimation of Nitrogen.** By C. ARNOLD (*Ber.*, 18, 806—812).—A modification of Will and Varentrapp's method for the combustion of nitrogenous compounds, in which the substance to be analysed is mixed with either of the following mixtures:—(1.) Equal parts of soda-lime, sodium thiosulphate, and sodium formate. (2.) 1 part of soda-lime, 2 of sodium thiosulphate, and 1 of sodium formate. The fore part of the tube is, as usual, filled with soda-lime, which should be sufficiently coarse to allow the gases to pass without the necessity of making a channel at the top of the tube. The second mixture yields the better results, which are very satisfactory. A. P.

**Modification of Kjeldahl's Method of Estimating Nitrogen.** By H. WILFARTH (*Chem. Centr.*, 1885, 17—19 and 113—115).—The process as described by Kjeldahl is often objectionable on account of the length of time required to complete the decomposition of certain organic substances. The presence of some metallic oxides, however, especially the oxides of iron, copper, and mercury, assists this decomposition in a marked degree. After numerous experiments the author selected the following method as the quickest and most trustworthy. A weighed quantity of the substance to be analysed is heated in a 200 c.c. flask with 20 c.c. of the acid mixture and 0.7 gram mercuric oxide until the decomposition is complete. After cooling it is diluted with water, the caustic potash solution and a solution of potassium sulphide added, distilled with a small quantity of zinc, and the distillate titrated for ammonia. This process often takes not more than one-eighth of the time required by the ordinary method. J. K. C.

**Kjeldahl's Method for Estimating Nitrogen.** By E. BOSSHARD (*Zeit. anal. Chem.*, 24, 199—201).—Kjeldahl recommends the addition of zinc shavings to the soda solution to diminish the bumping of the liquid. The author does not advise this proceeding, as it necessitates the employment of soda completely free from nitrates, and causes a fine spray to be formed which carries over a small quantity of soda into the distillate. If the gas flame is carefully regulated, no bumping need take place. (*Comp. Abstr.*, 1884, 364.) The accuracy of Kjeldahl's method is confirmed. S. R.

**Estimation of Phosphoric Acid.** By C. GLASER (*Zeit. anal. Chem.*, 24, 178—180).—The method depends on the fact that phosphoric acid when associated with calcium salts, &c., can be precipitated by magnesia mixture in the presence of ammonium citrate, provided sufficient sulphuric acid be added to convert all the lime salts into sulphate, and that no more ammonium citrate is used than is necessary to keep the calcium salts in solution. S. R.

**Estimation of Reverted Phosphoric Acid.** By A. PETERMANN (*Zeit. anal. Chem.*, 24, 175—178) and C. GLASER (*ibid.*, 180).—Replies to Mohr (this vol., p. 688).

**Estimation of Reverted Phosphoric Acid by the Oxalate Method.** By C. GLASER (*Zeit. anal. Chem.*, **24**, 181).—Good results can be obtained with phosphates containing only a small quantity of iron, by substituting a saturated solution of ammonium oxalate at the boiling temperature for the citrate solution usually employed. With guanos and iron phosphates this modification cannot be used.

S. R.

**Analysis of Phosphatic Manures.** By AUDOUARD (*Ann. Agronom.*, **11**, 141—142).—The author protests anew against the use of the “commercial” method of valuing raw phosphates in which the “ammonia precipitate” is reckoned as tricalcic phosphate. He shows by a record of 293 samples examined by this method and also by exact analysis, that the extent of the error is in most cases very considerable.

J. M. H. M.

**Alkaline Reaction of Glass.** By V. WARTHA (*Zeit. anal. Chem.*, **24**, 220).—By boiling a weighed quantity of different samples of glass with water in a silver dish, and then titrating with decinormal acid, the relative solubility of various kinds of glass was ascertained. There is a very wide range in the solubility of different varieties.

S. R.

**Estimation of Arsenic in Iron and Iron Ores.** By E. LUNDIN (*Chem. Centr.*, 1884, 954—955).—6 grams of iron or steel are dissolved in a beaker of 300 c.c. capacity by 70 c.c. of nitric acid (sp. gr. 1.2). When solution is complete, the liquid is transferred to a porcelain dish holding 150 c.c., about 40 c.c. of sulphuric acid are then added, and the solution evaporated on a sand-bath with frequent stirring until all the nitric acid is expelled, and volatilisation of sulphuric acid has commenced. When clots form a few c.c. more of sulphuric acid should be added. It has been proved that no arsenic is volatilised in this process. The mixture, now free from nitric acid, is placed in a retort holding about 300 c.c. and about 10 grams of finely powdered ferrous sulphate added in order to reduce the arsenic to arsenious acid. 70 c.c. of hydrochloric acid (sp. gr. 1.19) having been added the retort is connected with a 50 c.c. pipette which slopes into a beaker containing 300 c.c. of distilled water, so that the point is 12 mm. below the surface. The distillation is continued until the bulb of the pipette begins to get warm. The distillate is heated to 60—70°, and a current of hydrogen sulphide passed until precipitation has ceased. After expulsion of the excess of hydrogen sulphide by a stream of carbonic anhydride the precipitate is quickly washed and dried at 100—110°. It contains 60.98 per cent. of arsenic.

In the case of ores, 4 grams of the very finely powdered ore are digested in a warm place for 12 hours with 40 c.c. of nitric acid (sp. gr. 1.4), then treated with more nitric acid (sp. gr. 1.19). The liquid is evaporated to dryness with sulphuric acid, and subsequently treated in the foregoing manner.

W. R. D.

**Detection of Arsenic in Presence of Antimony.** By H. HAGER (*Chem. Centr.*, **51**, 955).—Arsenious compounds evolve arsenious hydride when heated with zinc and solutions of caustic alkali; the

gas can readily be detected by its reducing action on silver nitrate. Arsenic, antimony, and phosphorus compounds, formates, and oxalates, under like conditions, do not form any volatile compound which is capable of blackening paper soaked with solutions of silver nitrate; neither does the presence of any of these substances interfere with the reaction of arsenious compounds. Alcohol and ammonia do not interfere with the result; indeed, the deposition of metallic silver is rendered more evident when ammonia is present. The reaction is facilitated by having two metals in contact, instead of zinc alone zinc and magnesium should be employed. The method is advantageously used for the detection of arsenic in antimony salts, particularly in tartar emetic. For the latter purpose about 0.5 gram of powdered tartar emetic is mixed with 5–6 c.c. of potash solution (sp. gr. 1.16), and a few pieces of zinc and magnesium riband added. The mixture is then heated until gas is abundantly evolved, when a few more pieces of metal are introduced together with a fragment of ammonium chloride. The upper part of the tube or flask is loosely plugged with cotton-wool, and a slip of paper soaked in silver nitrate solution suspended or placed over the mouth. The tube is immersed in water at 50–70°. A browning or blackening of the paper occurs after about an hour when arsenic is present. The method which is frequently used for the detection of arsenic in tartar emetic, and which is based on the supposed insolubility of the antimony salt in alcoholic ammonia, and the solubility of the arsenious compound, is untrustworthy, for the tartar emetic is always to a greater or less extent dissolved. Consequently, the method is useless for the detection of traces of arsenic, for when the solution is mixed with hydrochloric and oxalic acids and evaporated on a strip of brass a dark stain does not necessarily indicate the presence of arsenic, although, as the arsenic compound is considerably more soluble than the antimony compound, fair quantities of arsenic produce a very deep red stain. Bettendorf's test for arsenic in tartar emetic, in which stannous chloride is used, gives good indications, but the zinc and alkali method is more delicate. In order to detect arsenious sulphide in the orange antimony sulphide, it should be extracted with a solution of ammonium sesquicarbonate in which antimony sulphide is insoluble, but the arsenious sulphide soluble. Ammonium bicarbonate should not be employed, since antimony sulphide is soluble in a solution of this salt.

W. R. D.

**Qualitative Separation of Tin, Antimony, and Arsenic.** By E. BERGLUND (*Zeit. anal. Chem.*, **24**, 221).—Slight modifications are given of the method previously described (*Abstr.*, 1884, 777).

S. R.

**Volumetric Determination of Tin.** By T. BENAS (*Chem. Centr.*, **51**, 957).—The author points out that the chief error in the volumetric determination of tin by iodine in acid or alkaline solution, is due to the action of the oxygen dissolved in the liquid or absorbed during the operation. In order to obtain constant results, the tin is dissolved in hydrochloric acid, diluted with water free from oxygen, and excess of iodine solution at once added. The liquid is then titrated with

sodium thiosulphate in the usual way. The solution to be titrated should contain about 0.25 gram of stannous salt in 100 c.c. of water.

W. R. D.

**Volumetric Estimation of Manganese.** By T. RAIMOND (*Chem. Centr.*, 1884, 156—157).—For the purpose of estimating manganese in iron, steel, and ferromanganese, 3 grams are warmed with 40 c.c. of nitric acid (sp. gr. 1.2) until dissolved. To the warm solution, 15 grams of potassium chlorate and 20 c.c. of nitric acid (sp. gr. 1.4) are added, and the mixture then heated until the chlorine is expelled. The precipitated manganese dioxide is collected, washed with hot water, transferred to a known quantity of an acid solution of a ferrous salt, and the unoxidised ferrous salt then titrated with potassium permanganate.

W. R. D.

**Volumetric Estimation of Iron.** By G. LIROSSIER (*J. Pharm.* [5], 11, 264—266).—The solution of ferric sulphate is rendered neutral with sodium carbonate, and acidified with a drop of sulphuric acid. A current of hydrogen sulphide is then passed into the liquid at a temperature of 50—80°. After complete reduction, which takes place rapidly, the excess of sulphide is mainly expelled by a few minutes' boiling. To remove the last traces, a few drops of mercuric chloride solution are added. After cooling, a little sulphuric acid is added, and the liquid titrated with permanganate.

J. T.

**Separation of Nickel and Cobalt.** By M. ILINSKI and G. v. KNORRE (*Ber.*, 18, 699—704).—The metals must be present as sulphates or chlorides. The solution is acidulated with hydrochloric acid and a hot solution of nitroso- $\beta$ -naphthol in 50 per cent. acetic acid added, until the whole of the cobalt is precipitated. The precipitate is washed first with cold, then with hot 12 per cent. hydrochloric acid, and finally with hot water. The precipitate is ignited with pure oxalic acid in a current of hydrogen and weighed as metallic cobalt.

Two compounds of cobalt with nitroso- $\beta$ -naphthol are described: a cobaltous compound,  $(C_{10}H_6NO_2)_2Co$ , is obtained as a brownish-red precipitate, on adding excess of a cobalt salt to a neutral aqueous solution of sodium nitroso- $\beta$ -naphthol; it is readily changed into the cobaltic compound by heating with acids. The cobaltic compound,  $(C_{10}H_6NO_2)_3Co$ , is obtained by adding a cobalt salt to an aqueous, alcoholic, or acid solution of nitroso- $\beta$ -naphthol, as a voluminous purple-red precipitate insoluble in dilute acids. The nickel salt,  $(C_{10}H_6NO_2)_2Ni$ , is obtained as a brownish-yellow precipitate on adding a nickel salt to a solution of nitroso- $\beta$ -naphthol in 50 per cent. acetic acid. It is sparingly soluble in water and alcohol, but hydrochloric and sulphuric acids decompose it readily, dissolving the nickel whilst nitroso- $\beta$ -naphthol separates.

A. J. G.

**Analysis of Tungsten Steel and Tungsten Iron.** By L. SCHNEIDER and F. LIPP (*Zeit. anal. Chem.*, 24, 292—293).—The sample is placed under water, and twice the quantity of bromine gradually added, with gentle heating; it is then mixed with nitric acid, and evaporated to dryness. The operation is repeated, and the mass then

dissolved in dilute nitric acid. The residue is fused with soda, the solution of the fused mass evaporated to dryness, and the mixture of silica and tungstic acid washed and weighed. This mixture is fused with five times its weight of hydrogen potassium sulphate, and the tungstic acid dissolved by treating the fused mass so obtained with a weak solution of ammonium carbonate. The silica is then washed and weighed, and the amount of tungstic acid present determined by difference.

S. R.

**Titration of Organic Matter in Water.** By A. PETIT (*J. Pharm.* [5], 11, 305—309).

**Examination of Potable Water.** By J. W. GUNNING (*Chem. Centr.*, 1884, 151—152).—The method recommended by the author for the chemical examination of water consists in adding to a litre of the water enough ferric chloride to correspond with about 5 mgrms. of iron. The ferric chloride should be as nearly neutral as possible. Under these conditions, ammonia, nitrites and nitrates are left in solution, whilst other nitrogenous substances are carried down with the precipitate of ferric hydroxide. By heating this with soda-lime the nitrogen of these compounds is obtained as ammonia. By this treatment cloudy water is completely clarified and yellow moor-water decolorised. The process has been applied with success on the large scale in Holland for the purification of drinking water, especially during diarrhoea and cholera epidemics. In the bacteriological examination of water, the author prefers to develop a pure culture in a liquid medium rather than in the solid medium recommended by Koch. The water to be tested is mixed with a clear sterilised yeast decoction. By sterilising this again, certain bacteria are either killed or rendered inactive, while the others from their superior vitality survive and develop. By a process of progressive sterilisation, beginning at low temperatures and gradually ascending, pure cultures are obtained.

W. R. D.

**Analysis of Vulcanised Caoutchouc and Estimation of the Sulphur in the same.** By B. UNGER (*Zeit. anal. Chem.*, 24, 167—175).—The sulphide of antimony used in vulcanising caoutchouc is obtained by decomposing a mixture of calcium sulphantimonite, thio-sulphate, and polysulphide with sulphuric acid. It therefore contains free sulphur (6—30 per cent.), antimony sulphide, and calcium sulphate (9—62 per cent.). The sulphur of the gypsum not being available for the vulcanisation, it is necessary to estimate the percentage of antimony and calcium, as well as of the sulphur in any sample of caoutchouc. The sulphur is best estimated by cutting up 0.5 gram of the sample into about 100 pieces, and mixing with 12 grams copper oxide and 2 grams soda, and heating strongly. The product is dissolved in nitric acid, evaporated, the antimonious acid formed separated, and the sulphuric acid in the filtrate estimated. The antimony is extracted by heating 1.5 gram of the sample with 10 grams of crystallised sodium sulphide and weighed as  $Sb_2S_3$ . For the calcium, 2.5 grams of the caoutchouc is incinerated, the ash dissolved in hydrochloric



acid, excess of ammonia added to precipitate antimony, and the calcium precipitated as oxalate.

Black vulcanised indiarubber is made with a different preparation; one, which is much used in England, consists of 66.55 talc, 21.1 red lead, 4.30 zinc oxide, and 8.05 sulphur. In this case, in estimating the sulphur as above described, lead sulphate will be formed, and must be dissolved by means of ammonium acetate. S. R.

**Analysis of Two Californian Wines.** By J. L. DE FREMERY (*Ber.*, 18, 426—427).

**Testing Wine for added Water.** By E. EGGER (*Chem. Centr.*, 1885, 71—72).—This method consists in estimating the quantity of nitrates present in the wine, the pure juice of the grape being absolutely free from these salts. In the case of white wines, 100 c.c. are evaporated to a syrup, and absolute alcohol added as long as it produces a cloudiness: the mixture is then filtered, decolorised with animal charcoal, and tested with sulphuric acid and diphenylamine. The author treats red wines first with lead acetate and then with magnesium sulphate before evaporation. To determine the nitric acid quantitatively Schulze-Tiemann's method is employed.

J. K. C.

**Estimation of Ethyl Nitrite in Spirit of Nitrous Ether.** By T. S. DYMOND (*Pharm. Trans.* [3], 15, 101—102).—The author advocates the use of the method based on the reaction of an acid solution of ferrous sulphate on the ethyl nitrite, wherein the volume of nitric oxide evolved is measured. The objection to this method is that it also estimates the free nitrous acid, the author, however, points out that probably nitrous acid in the presence of the alcohol in the preparation has the same therapeutic value as the ethyl nitrite, and therefore considers this objection unimportant.

D. A. L.

**Direct Estimation of Sugar in Beet.** By H. PELLET (*Chem. Centr.*, 1885, 150).—To extract the sugar from the carefully selected sample, the author employs a flask having the lower part of the neck contracted: this is filled with water up to the narrow part of the neck, where a porcelain stopper bored with several holes is allowed to rest; the weighed sample is then introduced, and the flask filled up to the 100 c.c. mark: it is then gently boiled for an hour or an hour and a half on a sand-bath, cooled, the liquid made up again to 100 c.c., filtered and tested in the ordinary way.

J. K. C.

**Application of the Densimeter to Cider Must.** By G. LECHARTIER (*Bied. Centr.*, 1885, 204—206).—The readings given by the densimeter when used for apple-juice are not trustworthy for estimations of sugar, as the sp. gr. of the must is largely dependent on the presence of tannin, pectin, &c., which accompany the sugar. Statistics concerning the composition of varieties of cider are given.

E. W. P.

**Detection of Sugar in Urine.** By G. BUCHNER (*Chem. Centr.*, 51, 958—959).—It is well known that urine which contains less than 1 per cent. of sugar if heated with Fehling's solution in the usual way, becomes opalescent and greenish or dark yellow in colour, but does not deposit cuprous oxide. According to the author, this is due to the presence of uric acid and creatinine, which should be removed by first adding to the urine a solution of copper sulphate (1 : 10), then warming and filtering from the precipitate. The filtrate containing excess of copper sulphate is next treated with Rochelle salt and potash solution and warmed. Under these conditions the smallest quantity of sugar is indicated by the precipitation of red cuprous oxide. W. R. D.

**Apparatus for the Estimation of Starch.** By R. REMPEL (*Ber.*, 18, 621—624).—The author describes, with sketches, an improved form of pressure-bottle, in which to heat under pressure the mixture of substance to be tested and tartaric acid solution. He also describes an air-bath with specially constructed inner bottoms to equalise the temperature. This bath is used for heating the pressure-bottle, and is much cleaner and more convenient to use than the paraffin-bath ordinarily employed. L. T. T.

**Estimation of Tartaric Acid in Wine Lees.** By V. OLIVIERI (*Gazzetta*, 14, 453—458).—Tartaric acid exists in wine lees as the potassium hydrogen and normal calcium salts; but besides these, in wines derived from a chalky soil, calcium sulphate is present; this reacts with the potassium hydrogen tartrate to yield potassium hydrogen sulphate, which dissolves, and normal calcium tartrate, which is precipitated. But as the market value of the material is proportional to the quantity of tartaric acid contained therein, it is desirable to ascertain with precision the quantity of tartaric acid existing as the soluble potassium and the insoluble calcium salt. The analytical methods proposed by Scheurer-Kestner and Scribani involve the precipitation of the calcium sulphate with the tartrate, thus raising the proportion of the latter and increasing the value of the material. To avoid this, a method of estimation is proposed in this paper based on the following processes:—(1.) Elimination by barium chloride of the sulphuric acid present as calcium sulphate. (2.) Precipitation of the calcium as oxalate, which is converted into sulphate, and from the result obtained the calcium corresponding with the sulphuric acid is subtracted, leaving as the remainder the calcium present in the form of the normal tartrate. (3.) Precipitation of the total tartaric acid as calcium tartrate, which is converted into sulphate, from which, after subtraction of the calcium tartrate determined above, the quantity of potassium hydrogen tartrate contained in the sample is deduced. The method of procedure is given in detail, together with the necessary calculations. The results obtained with artificial mixtures in imitation of wine lees were satisfactory. V. H. V.

**Test for Citric Acid.** By C. MANN (*Zeit. anal. Chem.*, 24, 201).—Citric acid if evaporated to dryness with glycerol, treated with

aqueous ammonia, and again dried, gives a deep green colour with hydrogen peroxide. Nitric acid when similarly treated also yields a green colour, but this changes to dark blue on warming. Tartaric and malic acids give no reaction. S. R.

**Natural Fats.** By C. DUBOIS and L. PADÉ (*Bull. Soc. Chim.*, **43**, 207—212).—The determination of the melting points and percentage of insoluble fatty acids of the following fats are given:—

	Raw fats.		Insoluble fatty acids.	
	Melting point.	Resolidifying point.	Per cent.	Solidifying at
Lard .....	33·2°	33°	93·4	42°
Veal fat.....	37·2	35·9°	94·54	42·7
Beef „ .....	42·2	41·5	94·20	44·2
Mutton fat ....	46·6	44·0	94·50	49·4
Butter .....	26·4	23·8	87·50—88·0	37·5
Margarin .....	39·6	38·4	95·6	45·6
Cocoa fat .....	31·6	30·2	94·73	48·8
Illipé fat .....	32·8	31·0	95·64	50·6

The microscopic appearances of the raw fats and their behaviour when viewed by polarised light are also described. The percentage of the insoluble fatty acids in butter is not perceptibly altered by keeping; in the case of two samples kept for eight months it only increased 0·14 and 0·08 per cent. Milk left in butter by insufficient washing does not cause any appreciable difference in the point of solidification.

A. P.

**Soap Analysis.** By A. GAWALOWSKI (*Zeit. anal. Chem.*, **24**, 219).

**Estimation of Butter in Cream.** By A. v. T. (*Bied. Centr.*, 1885, 199—200).—In America, where establishments exist solely for the sale of cream, it is necessary to know the quality of the cream; therefore samples are placed in vessels holding 113 cubic inches (yielding 1 lb. butter on an average), and nine of these vessels are fixed on a frame and rotated. This churns the cream, and the value of the bulk is estimated from the yield of butter thus produced.

E. W. P.

**Estimation of Oil in Cattle Cake.** By S. U. PICKERING (*Chem. News*, **51**, 181).—The following simple method is recommended as satisfactory. The sample along with some ether is placed in a closed vessel, which is immersed in boiling water for about half an hour. The extract is then filtered, and the residual mass washed with ether. The ether is distilled from the combined extract and washings, and the residual oil is dried at 100° and weighed.

D. A. L.

**Estimation of the Quinine Alkaloids.** By Y. SHIMOYAMA (*Arch. Pharm.*, **223**, 81—97).—The author finds that De Vrij's method of estimating quinine along with other related alkaloids is the best. The mixture of alkaloids (1 gram) is dissolved in alcohol containing 1.6 per cent. of sulphuric acid (20 grams), then 30 grams of pure alcohol are added. This addition appears to be absolutely necessary to prevent the precipitation of cinchonidine herapathite. The quinine is then precipitated as herapathite by means of an alcoholic solution of quinoidine-iodine sulphate. The method is only applicable when over 30 per cent. of quinine is present in the mixture, but the method is not of much value, as the necessary corrections cannot always be made.

C. Hielbig's proposed method of separating quinine from cinchonidine is impracticable except in cases where quinine is the only alkaloid present. All attempts to estimate quinine as herapathite in the presence of cinchonidine fail, as the latter when present in any considerable amount is partly precipitated. J. T.

**Separation of Casein from Albumin in Human Milk.** By F. HOPPE-SEYLER (*Zeit. physiol. Chem.*, **9**, 222—224).—This is an experimental refutation of the objection recently raised by Biedert to the method of separating casein from the albumin of human milk by dissolving magnesium sulphate in it to saturation. The author maintains the trustworthiness of this method, originally proposed by Tolmatscheff.

He also incidentally remarks that Schmidt-Mülheim, in a recent paper on the presence of cholesterin in milk (*Pflüger's Archiv*, **30**, 384), has overlooked the publication by Tolmatscheff and himself of the results of quantitative determinations of both cholesterin and lecithin in milk. C. F. C.

**Tests for Albumin in New and Old Urine.** By G. JOHNSON (*Pharm. J. Trans.* [3], **15**, 329).

**Determination of the Quantity of Ash in Tea.** By T. NIKITSKY (*J. Russ. Chem. Soc.*, 1884 [2], 297—298).—The statements, previously made by other chemists, are confirmed as to the fact that more costly teas contain less ash than the cheaper qualities. In all samples of (Chinese)\* tea analysed, the quantity of ash was in inverse relation to the quality, as indicated by the price, the percentage of ash being especially high in tea adulterated by admixture of leaves of *Epilobium angustifolium*. A. T.

\* Analyses of Japanese teas (*Chem. News*, **50**, 300) do not quite agree with this.—A. T.

## Technical Chemistry.

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**Different Modifications of Silver Bromide.** By H. W. VOGEL (*Ber.*, 18, 861—865).—A reply to the criticisms of Eder (*Sitzungsb. d. K. Ak. d. Wissensch.*, 1884, 1098) on the observations on the different modifications of silver bromide and their behaviour in different parts of the spectrum (*Abstr.*, 1883, 936). P. P. B.

**Natural Purification of Waters.** By F. EMICH (*Monatsh. Chem.*, 6, 77—94).—Rivers after receiving sewage, &c., gradually purify themselves as they proceed in their course. Several experimenters have shown that simple oxidation by the air is very slow, and the idea has been several times expressed that animal and vegetable organisms play an important part in the oxidation, but the question has not been decided by experiment. It is now shown that if the water be first sterilised by boiling, it may then be allowed to stand or be shaken with air, free from germs, without alteration taking place; direct oxidation, *i.e.*, without the intervention of organisms, does not occur. Practically the same conclusions have been arrived at by A. Müller, but his experiments seem to be almost unknown. The action of ozone or of hydrogen peroxide is but little more than that of air. H. B.

**Disinfection with Chlorine and Bromine.** By B. FISCHER and B. PROSKAUER (*Chem. Centr.*, 1884, 222—225).

**Manufacture of Potassium Dichromate.** By G. WACHTEL (*J. Russ. Chem. Soc.*, 1885 [1], 109—112).—The object of the investigation was to determine the behaviour of lime at a high temperature towards oxide of chromium and towards a mixture of the latter with potassium carbonate. In the first instance, a considerable difference is observed according as the oxide is used in the free state or in combination with ferrous oxide (as chrome iron), 90 per cent. of the former and only 30 per cent. of the latter being converted into chromate. The same experiments repeated on a large scale at Ouehkoﬀ and Co.'s works at Telaburga, showed that the best yield of chromate obtained corresponded with 20 per cent. of the oxide in the ore; another result of the action of lime on chrome iron being that part of the oxide of chromium (10 per cent.) acquires the property of dissolving in acids. Heating chrome iron in crucibles with potassium carbonate alone, and also with the addition of an equal quantity of lime to it, proved that the yield of chromic acid was almost twice as large in the latter case. Thus the simultaneous action of lime and potassium carbonate on the ore seems to be free from the defects of the process when either the one or the other are used alone. A. T.

**Chilian Boronatrocalcite.** By F. WITTING (*Chem. Centr.*, 1884, 147—148).—The boronatrocalcite from Maricunga (Chili) when sun-

dried contains on an average 30 per cent. of moisture and 24—25 per cent. of boric anhydride.

Specimens taken a few paces from the edge of the lagoon contained on an average 22 per cent. of  $B_2O_3$ . The deposit at Pederual is larger, but the mineral is about 1 per cent. weaker than that from Maricunga. Sulphur also occurs in Maricunga. The raw material contains calcium sulphate with from 55—58 per cent. of sulphur. A nitre deposit occurs on the Cerro de Torre (15,000 feet), but its capacity is not great. It is employed with pyrites from the Alpacarosa mine for the manufacture of sulphuric acid, which is produced in Caldera at the rate of 2000 kilos. ( $66^\circ B.$ ) a day. It is used for the preparation of boric acid from the boronatrocalcite, which is carried on to the extent of 5—6 tons a day. The Caldera boric acid contains 90.43 per cent. of crystallised boric acid, 2.76 per cent. of moisture, 2.05 per cent. of sodium sulphate, 4.12 per cent. of sodium chloride, and 0.64 per cent. of insoluble residue. W. R. D.

**Preparation of Ultramarine Blue from Silica.** By F. KNAPP (*J. pr. Chem.* [2], 31, 154—163).—It has been maintained that a species of ultramarine blue is obtainable from the separate constituents of kaolin. According to Gmelin, "equal parts of sodium carbonate, silica, and sulphur are mixed together, with addition of sufficient caustic soda to dissolve the silica; the mixture is then heated to and kept at a red heat for one hour; the bluish-grey product on roasting becomes a fine blue." Notwithstanding that these directions were closely followed, the author failed to obtain any blue product. Attention was paid to the manner of heating and mixing of the materials, but with no success. In order to determine the effect of various proportions of sodium carbonate and silica, weighed mixtures, consisting of different proportions of these two substances, were kept at a red heat for two hours, cooled and weighed; and the amount of expelled carbonic anhydride for each molecule of silica calculated. Only that product, containing 1 mol. sodium oxide combined with 1 atom of silica, possessed the necessary characteristics, namely, porosity and infusibility at a red heat. This fused product was powdered, mixed with sulphur, and kept for half an hour at a red heat; a highly porous pyrophoric mass was obtained, but all attempts to render it blue failed. All other experiments, varying the method of mixing, failed to yield the desired substance.

Rickmann also gives a method for the preparation of this substance (from silica without alumina), but like Gmelin he fails to describe the particulars of working, on which the success of the preparation almost entirely depends. H. P. W.

**Silvering of Glass.** By BÖTTGER (*Chem. Centr.*, 1885, 74—75).—The silvering liquid employed is made by dissolving 4 grams of pulverised silver nitrate in strong ammonia, adding 1 gram ammonium sulphate and 350 c.c. water. A solution of 1.2 grams starch or grape-sugar with 3 grams caustic potash in 350 c.c. of distilled water forms the reducing liquid. When used, equal volumes of the two liquids

are mixed together and applied to the surface of the substance to be coated.

J. K. C.

**Heat of Combustion of the Coal of Ronchamp.** By SCHEURER-KESTNER (*Compt. rend.*, **100**, 908—910).—The author has redetermined the heat of combustion of the coal of Ronchamp, and has obtained the value 9130 cal., a result agreeing with the determinations made in 1869. The composition of the combustible portion of the coal employed was C 89.09, H 5.09, N 1.30, S 1.03, O 3.49 = 100. In order to obtain comparable results, all calculations should be based on the combustible portion of the coal only, since the proportion of ash is so very variable. The author found that in the various fragments obtained by breaking one and the same lump of coal, the proportion of ash varied from 2.82 to 18.60 per cent.

C. H. B.

**New Method of Sugar Extraction.** By K. TROBACH (*Chem. Centr.*, 1885, 42).—The chopped or pulverised beetroot or sugar-cane is deprived of its water by means of alcohol vapour, and the sugar extracted from the residue by hot alcohol. The extract is then filtered through lime or chalk to remove acid salts. The object of this method is to obtain directly from the raw material the largest possible yield of crystallisable sugar without the formation of any inverted sugar, and to preserve in the desaccharised residue the whole of the salts, and thus render it more valuable as fodder.

J. K. C.

**Manufacture of Milk-sugar in Switzerland.** By J. KUNZ (*Pharm. J. Trans.* [3], **15**, 443—446).—Owing to the interference of the albumin, fat, milk-salts, and lactic acid, milk-sugar cannot be crystallised directly from whey in the same way as loaf-sugar is obtained from beet-juice. Therefore the whole success of the manufacture of milk-sugar rests on the efficient removal of these substances. In Switzerland after the removal of casein from fresh milk, the whey is heated to boiling, and a little sour whey is rapidly mixed with it; the fat rises, is skimmed off, and worked into butter. More sour whey is then added to the liquid, which is gradually heated to incipient boiling; the albumin coagulates, rises, and is removed. The remaining liquid is evaporated to a suitable syrupy consistency, and is allowed to cool slowly; the sugar separates in small crystals, "sugar-sand," whilst the milk-salts remain in solution. The "sand" is washed with very cold water, and is placed in bags to drain. The solutions of salts are used as fertilisers, for which purpose they are excellently adapted. The drained "sand" is again washed and drained, and then dissolved to saturation in boiling water; impurities are skimmed off, and the concentrated syrup run into large copper vessels to crystallise. Thin wooden sticks dip into the liquid, and act as nuclei for the crystals. The size, colour, &c., of the clusters of crystals depend, of course, on the strength and purity of the solution and on the rate of cooling. After 10 days the crystallisation is complete. The crystals obtained from the mother-liquor are worked up with a fresh quantity of "sand."

D. A. L.

**Notes on Milk.** By W. FLEISCHMANN (*Bied. Centr.*, 1884, 200—202).—Analyses of various samples of milk, evening and morning, ropy and preserved. E. W. P.

**Composition of Mares' Milk and Koumiss.** By P. VIETH (*Landw. Versuchs.-Stat.*, 31, 353—366).—The milk was obtained from mares exhibited at the Health Exhibition, 1884; the mares being a cross of Kirgish, Turkoman, and Tartar breeds, were 5—6 years old, and had foaled in April—May. The following analyses are of milk from all the mares at every milking during two days, the milking taking place every two hours (10—6), the total yield per mare being 4—5 litres:—

	Minimum.	Maximum.	Mean.
Sp. gr. ....	1·0335	1·0360	1·0349
Water.....	89·74 p. c.	90·41 p. c.	90·06 p. c.
Fat .....	0·87 „	1·25 „	1·09 „
Albuminoids ....	1·71 „	2·11 „	1·89 „
Sugar .....	6·30 „	6·82 „	6·65 „
Ash (soluble) ...	0·06 „	0·11 „	0·08 „
„ (insoluble after ignition)	0·20 „	0·25 „	0·23 „

In the next table the composition of milk from various mares milked at the same time is given:—

	Minimum.	Maximum.	Average.
Sp. gr. ....	1·0344	1·0358	1·0350
Water.....	89·88 p. c.	90·46 p. c.	90·13 p. c.
Fat .....	0·62 „	1·18 „	0·94 „
Albuminoids ....	1·50 „	1·83 „	1·65 „
Sugar .....	6·70 „	7·21 „	6·98 „
Ash (soluble)....	0·04 „	0·10 „	0·07 „
„ (insoluble)...	0·20 „	0·27 „	0·23 „

An examination of the complete table shows that lactation and weather have a considerable influence on the composition of the milk. A final set of analyses shows the influence of feeding, the normal food being hay, clover, oats, and “Good’s food.” Whilst during the experiment the food was restricted to hay and Good’s food, there was an increase in all constituents except ash and water.

At Orenburg, mares’ milk is condensed, 2·33 per cent. of sugar being added. Analyses are given.

Mares’ milk begins to ferment during warm weather in 24 hours, the resulting liquid being called koumiss. In this condition, the peculiar taste of the original milk is lost and a new one acquired. Analyses of koumiss in three different stages of preparation are given. There was some difficulty found in the estimation of the casein, so that some doubt as to the accuracy of the determination (by difference) of the sugar exists. One analysis, for example, gave the following results:—Water 92·42 per cent., alcohol 3·29, fat 1·20, casein 0·79, albumin 0·32, lactoprotein and peptone 0·76, lactic acid 1·00, sugar 0·0, ash (soluble



0.12, (insoluble) 0.23. Other analyses show a percentage of 0.19—0.69 of sugar. Koumiss is also made from condensed milk, when 5.13 per cent. of sugar is to be found. E. W. P.

### **Medicinal Properties of the Root Bark of the Pomegranate.**

By I. KAMNITZER (*Chem. Centr.*, 1884, 43).—The root contains, in addition to a tannic acid, mannitol, starch and calcium oxalate, four alkaloïds which have lately been described by Tanret. A small dose of the bark produces colic-like symptoms, whilst a large dose brings on most serious results, giddiness, deafness, trembling of the limbs, vomiting, purging, and inflammation of the stomach and intestines. This last result is found to be due to the large amount of tannin present, as on its removal the violent local disturbances in the stomach are absent. As a remedy for tape-worm, the fresh roots should be macerated in the cold for 1—2 days, the liquid then contains pelletierine tannate, the essential constituent. A. P.

**Preparing Yellow Azo-colouring Matters.** (*Dingl. polyt. J.*, 255, 404.)—A patent has been taken out by the *Société Anonyme des Matières Colorantes de St. Denis* in Paris for the production of azo-dyes by the action of para- or meta-diazobenzoic acid on diphenylamine or monobenzylaniline. The resulting colouring matters dye vegetable fibres with a yellow colour, which resists soaping at 60°. The colour obtained with the meta-acid is yellower than that produced by the action of the para-acid on diphenylamine or monobenzylaniline. It is fixed in the following manner:—The dye is thickened with starch-paste or gum tragacanth, and treated with soda, potash or ammonia to convert the base into a salt. This is then boiled, allowed to cool and treated with an excess of acetic acid to liberate the colouring matter in a form well adapted for the fixation of the dye on cottons. The best mordant is chromium acetate. After printing, the fabric is steamed and soaped at 60°. These dyes may be used with advantage in conjunction with alizarin reds.

D. B.

**Preparation of Galleïn.** By O. GÜRKE (*Dingl. polyt. J.*, 255, 452).—Instead of preparing galleïn by heating pyrogallol with phthalic anhydride, the author employs gallic acid, which is resolved into pyrogallol and carbonic anhydride when heated with phthalic anhydride. For this purpose, 37.6 kilos. of crystallised gallic acid are heated in an oil-bath to 220—235° with 17 kilos. of phthalic anhydride, until the melt becomes solid. It is then thrown into water, evaporated to dryness, and dissolved in alcohol. On expelling the latter by evaporation, galleïn remains. This is converted into cöruleïn by the usual process.

D. B.

**Preparation of Indigo.** By H. MÜLLER (*Dingl. polyt. J.*, 255, 356).—On chlorinating benzaldehyde in the presence of dehydrating agents, metachlorobenzaldehyde is obtained. It forms a colourless liquid of sp. gr. 1.246 at 15°, boils at 206°, and is converted into metachlororthonitrobenzaldehyde when treated with nitric acid, potassium nitrate, and sulphuric acid. The nitro-compound crystallises from

alcohol in yellow needles melting at 60°. When dissolved in acetone and treated with dilute soda-ley, it deposits a crystalline powder of chlorindigotin, which, like indigo, is insoluble in water, alcohol, ether, weak acids, and alkalis. By the action of reducing agents on chlorindigotin, a vat is obtained which can be worked like an ordinary indigo vat. Indigo can be obtained by the action of nascent hydrogen (comp. Abstr., 1884, 1028). D. B.

**Investigation of Bone-meal.** By J. KÖNIG (*Dingl. polyt. J.*, **255**, 301—303).—The author has found as much as 9 per cent. of moisture in samples of bone-meal. He analysed a number of samples of bone-meal, and obtained the following percentages calculated on anhydrous substance :—

*A. Steamed Bone-meal treated by Old Process for Removal of Fat.*

	Fat.	Gelatine, &c.	N.	Ash.	P.
1. Boiled and steamed with pressure of 1 atmos. ....	12·77	31·13	4·35	56·10	21·04
Ditto, another quality.....	11·98	29·81	4·41	58·21	22·15
2. Ditto .....	9·70	30·37	4·49	59·93	21·65
3. Steamed with pressure of 1·5 atmos.	10·56	33·08	4·45	56·36	23·06
4. Ditto .....	10·76	32·26	4·49	56·88	22·11

*B. Steamed Bone-meal treated by New Process for Removal of Fat.*

5. Fat removed with benzene vapour, according to Leuner, not steamed..	8·53	33·98	4·87	57·49	22·05
6. Ditto, but steamed for 10 minutes with a pressure of 3 atmos. ....	2·29	30·24	4·54	67·47	26·49
7. Fat removed with benzene at a pressure of 1·25 atmos., and subsequently steamed at a pressure of 1·5 atmos. (Seltsam's process) ....	6·34	32·15	<i>fine</i> 4·75	61·51	22·72
8. Fat removed with benzene in a vacuum; pressure under 1 atmo. (Richter's process) .....	4·73	36·78	<i>coarse</i> 4·45	58·49	22·15
	5·43	31·33	4·46	63·24	22·91

The samples of meal prepared by the new process contain less fat and more nitrogen, and are therefore more valuable for agricultural purposes than the meals produced by the old process. D. B.

**Vegetable Leather.** By M. BAUER, L. BROUARD, and J. ANCEL (*Chem. Centr.*, 1884, 798—799; from *D. Ind. Ztg.*).—A mixture of 3 kilos. gutta-percha, 900 grams sulphur, 1 kilo. raw cotton, 600 grams zinc white, 100 grams colcothar, and 250 grams antimonie oxide yields, when vulcanised with steam, a very good substitute for leather. The necessary constituents in this mixture are gutta-percha and sulphur, the remainder may be varied or replaced by others according to the character of the leather required. L. T. T.

**Harmless Soldering Mixture.** (*Chem. News*, 51, 147.)—When soldering the tins in canning provisions, it is proposed to substitute for the noxious zinc chloride a harmless mixture of 1 part lactic acid, 1 part glycerol, and 8 parts of water. This mixture is patented and is in use.

D. A. L.

**Novelties in Explosives.** (*Dingl. polyt. J.*, 255, 337—344.)—For the production of gunpowder containing cotton, J. Nordenfelt and V. A. Meurling propose to prepare a carbonaceous substance from cotton, woody fibres, or similar substances, by treating them in a loose form with hydrochloric acid gas, whereby the fibre is converted into a brittle substance. This is thoroughly mixed with the proper amount of a saturated solution of sulphur in carbon bisulphide in a closed vessel provided with a mechanical agitator. The dry mixture of carbon and sulphur is saturated with an aqueous solution of potassium nitrate, and the water evaporated off at a gentle heat. The powder is then finished according to the usual method.

F. W. Gilles proposes to manufacture explosive compounds by treating molasses with a mixture of nitric and sulphuric acids. He obtains the explosive in two forms, which he calls solid and liquid nitro-molasses. In both cases 380 grams molasses, 1000 grams fuming nitric acid, and 2000 grams concentrated sulphuric acid are mixed together. The product when washed first with cold then with warm water, deposits a precipitate of a grey-yellow or whitish colour, and can be used at once as an explosive material. To obtain the liquid explosive, the nitro-molasses is brought to a composition corresponding to 34 parts carbon, 54 parts oxygen, and 12 parts hydrogen, nitrogen, and salts. When the molasses contains less oxygen and carbon than the above proportion, it is treated in open vessels with lead peroxide and carbon bisulphide, and the mixture is allowed to ferment at a temperature not exceeding 130°. The prepared molasses is then nitrated. When the molasses contains less oxygen than the proportion stated above, it is treated by oxygen gas forced into it under pressure in closed vessels. The fluid nitro-molasses when heated slowly boils at between 180° and 200°, and detonates between 220° and 250°, and can be mixed with any absorbent.

According to a process invented by S. R. Divine, dry potassium chlorate is filled into cartridges made of cloth, paper, or other porous materials, and saturated with heavy coal-tar oil in such proportions as to form an explosive compound. To facilitate the saturation of the potassium chlorate with oil, the latter is mixed with carbon bisulphide or other volatile fluid, and to increase the sensitiveness of the explosive, sulphur dissolved in carbon bisulphide is added in proportions such as will supply from 1—3 per cent. of sulphur on the total quantity of potassium chlorate present.

D. B.

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## General and Physical Chemistry.

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**Spontaneously Reversible Lines in Spectra.** By A. CORNU (*Compt. rend.*, 100, 1181—1188).—This paper is mainly a discussion of known facts, with special reference to the problem of deducing the distribution and relative intensities of the lines in the spectrum of an incandescent vapour from its chemical composition. The author points out that lines which form periodic groups are almost invariably spontaneously reversible. These lines close up towards the more refrangible end of the spectrum, and diminish in intensity. He finds that in the spectra of many metals the spontaneously reversible lines follow sensibly the same laws of distribution and intensity as the lines of hydrogen, and it would seem that this law of succession of the spectral lines common to so many series may possibly be expressed by the same function, which may be termed the hydrogenic function.

C. H. B.

**Use of Carbon Bisulphide in Prisms.** By H. DRAPER (*Amer. J. Sci.*, 29, 269—277).—Although carbon bisulphide has a higher refractive power than glass, yet its use in spectroscopic observations has been much restricted, owing to the spectra produced by prisms filled with this material being ill defined. The result is due to striæ, caused by convection currents produced by inequality of temperature. These can be prevented by an active rotation of the liquid, and by maintaining the temperature of the prism constant; the former being effected by the author by a small propeller wheel driven by an electric motor, the latter by a temperature regulator. The constant temperature also prevents the changing of the refractive energy of the liquid, and the continual shifting of the position of the spectral lines either in one direction or the other. The adoption of these devices is of great practical value, inasmuch as a bisulphide prism, whilst giving seven-eighths as much dispersion as six flint prisms, gives four times the light in the entire spectrum and eight times the light in the region near G. For photographic purposes, the carbon bisulphide prism should replace the train of glass prisms, and even gratings.

V. H. V.

**New Constant Galvanic Element.** By E. VORWINKEL (*Dingl. polyt. J.*, 256, 218—221).—An adaptation of potassium or sodium permanganate to the new chromic acid element described by the author in a previous communication (*ibid.*, 255, 431, and 256, 23).

D. B.

**Battery with Two Liquids.** By A. DUPRÉ (*Compt. rend.* 100, 987—989). The outer cell of a Bunsen element, that is, the cell containing the zinc, is filled with dilute acid, a solution of potassium hydrogen sulphate, or other similar liquid, and the inner cell containing the carbon is filled with nitric acid, in which are dissolved 75 grams of potassium dichromate per litre. No oxides of nitrogen are given off, and the battery will work for at least 15 hours without appre-

cial deterioration; the electromotive force depending on the concentration of the acid. Instead of using nitric acid, the inner cell may be filled with a solution obtained by dissolving 510 grams of sodium nitrate in 600 c.c. of water, and adding successively 400 c.c. of ordinary sulphuric acid and 60 grams of potassium dichromate. The electromotive force with this solution is 1.5—1.7 volts.

C. H. B.

*Note by Abstractor.*—The effect of potassium dichromate in preventing the evolution of nitrogen oxides from a Bunsen or Grove's battery has been known for some time.

**Suppression of Nitrous Fumes from the Bunsen Battery.**

By A. D'ARSONVAL (*Compt. rend.*, 100, 1165—1167).—The author points out that the use of potassium dichromate to absorb the oxides of nitrogen given off in the Bunsen cell was proposed by Ruhmkorff in 1869.

The author employs a rectangular Bunsen cell, in which the nitric acid is replaced by a solution of cupric chloride in hydrochloric acid. The copper is deposited on the carbon plate, but in the presence of air and hydrochloric acid is almost instantly dissolved. Its solution is accelerated by increasing the surface of the carbon, or by blowing air into the liquid. This cell has an electromotive force of about 1.5 volt, and a flat cell of Ruhmkorff's model gives a current of 8 to 12 ampères.

C. H. B.

**New Arrangement of the Thermo-electric Pile.** By CLAMOND and J. CARPENTIER (*Compt. rend.*, 100, 985—987).

**New Pile, or Auto-accumulator.** By JABLOCHKOFF (*Compt. rend.*, 100, 1214—1216).—This is a pile with three electrodes, the first of which is an oxidisable metal, the second carbon, or a metal which oxidises with difficulty, and the third porous carbon, which is surrounded by air.

Fragments of an oxidisable metal, such as sodium, zinc, or iron, are placed in a flat leaden tray, and the latter is then filled up with some porous material, such as sawdust. If sodium is used, the sodium oxide formed is sufficiently hygroscopic; but if zinc or iron is employed the sawdust must be moistened with a solution of calcium chloride. A series of tubes of porous carbon is placed on the top of the porous substance.

When the circuit is open, local currents are set up between the oxidisable metal and the electrode on which it is placed, and the latter is polarised until its potential reaches that of the metals, at which point the action ceases, or is reduced to a minimum. If now the electrode thus polarised is connected with the carbon electrode, the discharge commences, and at the same time local currents are again set up, and recharge the electrode as fast as it is discharged.

The electromotive force varies with the nature of the oxidisable metal; with sodium amalgam, it is 2.2 volts, with zinc 1.6, with iron 1.1. The internal resistance of an element 0.1 m. square varies from

0.25 to 0.5 ohm, according to the thickness of the spongy layer and its degree of humidity.

C. H. B.

**Electrical Conductivity of Solid Mercury and other Metals at Low Temperatures.** By CAILLETET and BOUTY (*Compt. rend.*, 100, 1188—1191).—The electrical resistance of most pure metals decreases regularly with a reduction of temperature from 0° to -123°, and the coefficient of variation is practically the same in all cases.

The resistance of mercury decreases at the point of solidification in the ratio of 4.08 : 1, and the resistance of solid mercury decreases with the temperature. Between -40° and -92.13° it is represented by the formula—

$$R_t = R_{-40} \frac{1 + at}{1 - 40a},$$

Where  $a = 0.00407$ , a value closely approaching that for other metal. The values of  $a$  for several metals are as follows:—

	$a$ .	Limits of temperature.
Silver .....	0.00385	+ 29.97° to - 101.75°
Aluminium ....	0.00388	+ 27.7 to - 90.57
Magnesium ....	0.00390	0 to - 88.31
Tin .....	0.00424	0 to - 85.08
Copper.....	0.00418	0 to - 58.22
" .....	0.00426	- 68.65 to - 101.30
" .....	0.00424	- 113.08 to - 122.82

The variation in the resistance of platinum and iron differs from that of other metals below zero as well as above. The formula  $R_t = R_0(1 + at)$  holds good in the case of iron when  $a = 0.0049$ , but in the case of platinum the value of  $a$ , which is 0.0030 at 0°, increases as the temperature falls, and becomes 0.00342 at -94.57°, or in other words, the lower the temperature the more closely does the value of the coefficient for platinum approach that for other metals.

C. H. B.

**Conductivity of Cetyl Alcohol.** By A. BARTOLI (*Gazzetta*, 14, 522—526).—Cetyl alcohol at temperatures below 15° shows no sign of electric conductivity, so that it might be used as an insulator, but its conductivity gradually increases, reaching its maximum at 45°; then it very rapidly decreases to the melting point 48°, and reaches the minimum at 50°. On raising the temperature still further, its conductivity again slowly increases. On cooling, the phenomena are presented in the reverse order. The same result is obtained when electrodes of copper, zinc, or silver are substituted for those of platinum; frequent melting and solidification do not alter the relative conductivity. Several other organic substances show the same phenomena.

V. H. V.

**Measurement of Strong Electrical Currents.** By J. TROWBRIDGE (*Amer. J. Sci.*, 29, 236—237).—The author has recently employed the cosine galvanometer for measuring strong currents, in the following

manner:—The galvanometer is mounted so that the needle is at the centre of a large circle of wire, the plane of which is vertical and is in the magnetic meridian. When the current from a dynamo machine is passed through the large vertical coil, which may consist of a single wire, the arrangement answers as a tangent galvanometer. The movable coil of the cosine galvanometer is then connected with a Daniell cell of known electromotive force. In the same circuit is placed a resistance so large that the battery resistance can be neglected, and, the poles being joined in such a manner that the deflection produced by the coil of the cosine galvanometer shall be opposite to that produced by the current from the dynamo machine in the large outer coil, the coil of the cosine galvanometer is inclined until the needle is again brought to zero. Then, if  $F$  and  $F'$  represent the forces produced at the centre of the coils by the current from the dynamo, and by the Daniell cell;  $S$  and  $S'$  the respective currents;  $r$  and  $r'$  the radii;  $n$  and  $n'$  the number of coils in the two galvanometers, and  $H$  the horizontal force of magnetism,

$$F = \frac{2\pi nSH}{r} = F' = \frac{2\pi n'S'H}{r'} \cos \alpha, \text{ or } S = \frac{S'n'}{n} \frac{r}{r'} \cos \alpha.$$

The strength of the current is thus obtained in terms of the current from the standard Daniell cell, and the method is independent of the strength of the earth's magnetism. The diameter of the outer coil can be diminished by passing the current through one coil in one direction, and through an inside coil in another. B. H. B.

**Trustworthiness of Alternating Currents for Measuring Electrical Resistances.** By W. OSTWALD (*J. pr. Chem.* [2], 31, 219—223).—Doubt has been cast upon the application of Kohlrausch's method to organic substances, it being alleged that in the case of acetic acid, for instance, the ethane and carbonic anhydride liberated by the current cannot recombine during the passage of the alternate current. But ethane and carbonic anhydride are only secondary products, and cannot be formed owing to the rapidity of change of current. Experimental proof of the trustworthiness of the method is shown by a constant result being obtained with various strengths of current, alternating at different speeds, and by direct comparison of results given by a number of organic and inorganic substances, with direct and alternating currents. H. B.

**Relation of "Peltier's Heat Effect" to the Available Energy of a Galvanic Element.** By A. GÖCKEL (*Ann. Phys. Chem.*, 24, 618—642).

**Calorimetric Study of the Effect of Tempering and Hammering on Cast Steel.** By OSMOND (*Compt. rend.*, 100, 1228—1240).—The samples of steel used in these experiments were: (1) extra mild steel, carbon 0.17 per cent.; (2) medium steel, carbon 0.54 per cent.; (3) tool steel, carbon 1.17 per cent.; (4) Swedish white iron, carbon 4.10 per cent. Each of these specimens was subjected to three different kinds of treatment, namely, annealing,

hammering, and tempering, and samples in each state were dissolved in a neutral solution of cuprous ammonium chloride in a calorimeter. The rise of temperature produced by the solution of 1·5 gram of metal in 500 c.c. of copper solution, is given in Table I, and the ratios in Table II:—

I.			
	Annealed.	Hammered.	Tempered.
1.....	2·151°	2·247°	—
2.....	2·111	2·207	2·222°
3.....	1·895	2·018	2·056
4.....	1·419	—	1·632

II.			
	Annealed.	Hammered.	Tempered.
1.....	1·000°	1·045°	—
2.....	1·000	1·045	1·052°
3.....	1·000	1·065	1·084
4.....	1·000	—	1·150

It is evident that hammering, and still more tempering, produce an increase in the amount of heat developed, and the increase is greater the greater the proportion of carbon in the steel. The iron is probably converted into an isomeric modification in tempering. C. H. B.

**Combustion of Explosive Mixtures of Coal-gas and Air.** By A. WITZ (*Compt. rend.*, 100, 1131—1132).—The theoretical temperatures and pressures produced by the explosion of mixtures of coal-gas and air, as calculated from the heat of combustion of coal-gas, are as follows:—

	At const. vol.		At const. pres.	
	Temp.	Pres.	Temp.	Pres.
1 vol. of gas + 6 vols of air ..	2064°	8·6 atmos.	1596°	6·8 atmos.
1 vol. of gas + 10    "    " ..	1514°	6·5    "	1169°	5·3    "

Any difference between the calculated and observed pressures must be attributed to the action of the walls of the explosion vessel, since Mallard and Chatelier have shown that carbonic anhydride and water do not dissociate below 1800° and 2500° respectively in explosions.

C. H. B.

**Calorimetric Investigations.** By F. STOHMANN (*J. pr. Chem.* [2], 31, 273—306).—This paper contains an account of some improvements in the calorimeter described by the author in a former communication (*Abstr.*, 1879, 586). The results of the determination of the heats of combustion of a great variety of substances are then given, such as animal and vegetable fats, butter, albuminoids, meat, bread, carbamide, uric acid, hippuric acid, glycocine, asparagine, carbohydrates, mannitol, and its isomeride, erythrol, some of the solid paraffins, naphthalene, and anthracene. Also the heats of combustion of some of the higher fatty acids, of oxalic acid, and some of its



homologues, of tartaric and citric acids, of benzoic, salicylic, and phthalic acids, of cetyl alcohol and of glycerol, phenol, resorcinol, pyrocatechol, pyrogallol, and thymol, and finally of cetyl palmitate and trimyristin. Many of these results differ from those obtained by v. Rechenberg (Abstr., 1881, 135). P. P. B.

**Influence of Dilution on the Coefficient of Reduction of the Freezing Point of Various Aqueous Solutions.** By F. M. RAOULT (*Compt. rend.*, 100, 982—984).—The author has investigated the effect of dilution on the freezing points of aqueous solutions of salts, acids, bases, and organic compounds, the results being represented by curves which have for abscissæ the reduction of the freezing point  $C$ ,

and for ordinates the coefficient of reduction  $\frac{C}{P}$ , where  $P$  is the weight

of the anhydrous substance in 100 grams of water. The curves thus obtained are simple curves resembling hyperbolas, the most curved portion being near the axis of the ordinates, with its convex side away from the axis of the abscissæ, whilst the least curved portion extends away from the axis of the ordinates, and approximates more and more closely to a straight line. When the freezing point is below  $-2^{\circ}$ , or the solution contains more than a gram-molecule in 2 litres, the latter portion of the curve differs very little from a straight line which runs parallel with or away from the axis of the abscissæ, or else approaches it. When the line diverges from or is parallel with the axis of the abscissæ, the substance dissolves in accordance with Blagden's law, and exists in solution in the hydrated or anhydrous state respectively. The convergence of the curve towards the axis of the abscissæ indicates that when the concentration of the solution passes a certain point, the dissolved molecules begin to aggregate and form more complex molecules. If a fresh quantity of any substance is added to a non-saturated solution of that substance, one portion will unite with the substance already dissolved, forming more condensed molecules without lowering the freezing point, whilst the other portion dissolves in the water in its original state, and increases the reduction of the freezing point, in accordance with Blagden's law. The two portions are proportional to the relative quantities of water and substance already existing in the solution. It follows that the

coefficient of reduction  $\frac{C}{P}$  diminishes, and the diminution is propor-

tional to the increase in the reduction of the freezing point. The corresponding curve approaches the axis of the abscissæ, as in the case of sodium nitrate, and if sufficiently prolonged will cut the axis of the ordinates at a point, the ordinate of which represents the coefficient of reduction of the substance supposed to have dissolved without condensation, or, in other words, it represents the *normal coefficient of reduction*. The values thus obtained agree better than any other values with the general laws previously enunciated.

The portion of the curve in the neighbourhood of the axis of the ordinates corresponds with solutions so dilute that they freeze between  $0^{\circ}$  and  $-1^{\circ}$ . Each curve between these limits has its own particular form, and diverges more or less rapidly from the axis of the ordinates,

tending to become tangential to it. This shows that the coefficient of reduction of any substance is increased by dilution. But such an increase indicates an increase in the number of molecules, and consequently points to a partial decomposition of the dissolved substance. It follows that all substances are more or less decomposed in very dilute solutions. Berthelot has already shown that this is the case with many salts, and the author's results prove that it also takes place, although in a much lower degree, with sulphuric acid, alcohol, tartaric acid, sugar, &c.

C. H. B.

**Relation between Critical and Boiling Points.** By A. BARTOLI (*Gazzetta*, 14, 540—543).—Pawlewski has shown that the difference between the boiling point and critical temperature for the ethereal salts of the acetic acid series is a constant (Abstr., 1883, 276), a generalisation which Nadejdine has confirmed for the olefine hydrocarbons (*Beiblätter, Ann. Phys. Chem.*, 7, 678). In this note, the author shows that this relation does not represent a physical law, but is purely empirical and accidental, inasmuch as it does not hold good for boiling points under pressures other than the atmospheric. Tables are given which show that the difference between the critical temperature and the boiling points taken at 60° and 760 or 1260 mm. pressures are very variable.

V. H. V.

**Mendeléeff's Formula for the Expansion of Liquids, and Thorpe and Rücker's Formula for Determining the Critical Temperature of Liquids from their Coefficient of Expansion.** By A. BARTOLI and E. STRACCIATI (*Gazzetta*, 14, 527—540).

**Critical Temperatures and Specific Volumes of Paraffin Hydrocarbons from Pennsylvania Petroleum.** By A. BARTOLI and E. STRACCIATI (*Gazzetta*, 14, 548—558).

**Dissociation Tension of Ammonium Carbamate.** By G. ERCKMANN (*Ber.*, 18, 1154—1156).—These experiments were made in a Hofmann's vapour-density apparatus. The dissociation tension of ammonium carbamate is 361 mm. at 47·25°, 562·8° mm. at 54·75°, and 632·2 mm. at 56·5°.

A. J. G.

**Dissociation Tension of Ammonium Carbamate.** By A. NAUMANN (*Ber.*, 18, 1157—1159).—The agreement of the results in the preceding Abstract with those obtained earlier by the author (this Journal, 1871, 1195) is pointed out. The much higher results obtained by Isambert (Abstr., 1882, 270), who mixed ammonia (2 vols.) and carbonic anhydride (1 vol.), are attributed to insufficient time having elapsed to allow combination to take place before determining the tension.

A. J. G.

**Liquefaction of Oxygen.** By L. CAILLETET (*Compt. rend.*, 100, 1033—1035).—When a glass vessel containing compressed oxygen is surrounded by liquid ethylene, previously cooled to  $-70^{\circ}$  in a copper helix by means of methyl chloride, and the ethylene is caused to

evaporate rapidly by directing upon it a jet of cooled air, the temperature obtained is below the critical point of oxygen, and the latter liquefies readily in the glass tube, showing a perfectly distinct meniscus. The temperature of the ethylene, as indicated by a hydrogen thermometer, was  $-123^{\circ}$ . C. H. B.

**Liquefaction and Solidification of Methane and Nitric Oxide.** By K. OLZEWSKI (*Compt. rend.*, **100**, 940).—The methane employed was obtained either by treating sodium acetate with soda-lime, or by the action of the zinc-copper couple on a mixture of methyl iodide and alcohol. The following table gives the temperature of the liquefied methane under various pressures:—

Pressure.	Temperature.	Pressure.	Temperature.
54.9 atmos.	— $81.8^{\circ}$ (crit. point)	6.2 atmos.	— $138.5$
49.0 "	— $85.4$	2.24 "	— $153.8$
40.0 "	— $93.3$	1.00 "	— $164.0$
26.3 "	— $105.8$	80 mm.	— $185.8$
21.4 "	— $110.6$	5 "	— $201.5$
11.0 "	— $126.8$		

When the pressure is reduced below 80 mm., the liquefied methane begins to solidify, and if the reduction of pressure is continued, it forms a white snow-like mass.

Nitric oxide was obtained by heating ferrous sulphate with dilute nitric acid, and was liquefied by means of ethylene boiling under low pressure, care being taken to purify the nitric oxide from higher oxides of nitrogen, and to prevent the access of air or oxygen. The relation between the temperature of the liquefied gas and the pressure is given in the following table:—

Pressure.	Temperature.	Pressure.	Temperature.
71.2 atmos.	— $93.5^{\circ}$ (crit. point)	10.6 atmos.	— $129.0^{\circ}$
57.8 "	— $97.5$	5.4 "	— $138.0$
49.9 "	— $100.9$	1.0 "	— $153.6$
41.0 "	— $105.0$	138 mm.	— $167.0$
31.6 "	— $110.0$	18 "	— $176.5$
20.0 "	— $119.0$		

Nitric oxide begins to solidify at  $-153.6^{\circ}$ , under a pressure of 138 mm., and forms a snow-like mass. At 71.2 atmos., the meniscus becomes indistinct, but does not completely disappear.

When the curve of liquefaction of nitric oxide is compared with those of nitrogen, carbonic oxide, oxygen, and methane, especially the latter, it is seen that the pressure increases much more rapidly with an increase of temperature in the case of nitric oxide, than with the other gases. This difference is probably due to an increase in the complexity of the nitric oxide molecule at low temperatures.

Cailletet has obtained results which, so far as they go, confirm those obtained by Olzewski. He has also found that the temperature produced by the rapid evaporation of liquid methane is sufficiently low to liquefy oxygen immediately. C. H. B.

**Tensions and Critical Points of Some Vapours.** By C. VINCENT and J. CHAPPUIS (*Compt. rend.*, **100**, 1216—1218).—The critical temperature of hydrogen chloride is between  $51^{\circ}$  and  $51.5^{\circ}$ , a result which confirms the value given by Ansdell (*Proc. Roy. Soc.*, **34**, 113).

The critical point of methyl chloride is about  $141.5^{\circ}$ . If the methyl chloride is mixed with a small quantity of a permanent gas, the pressure at the critical point increases with the proportion of the permanent gas, but the temperature is always between  $141^{\circ}$ — $142^{\circ}$ .

The observed vapour-tensions agree with those calculated by Regnault's formula up to  $35^{\circ}$ , but at  $90^{\circ}$  there is a difference of 1 atmos., which is increased to 2 atmos. at  $141^{\circ}$ . C. H. B.

**Phenomena which Accompany the Evaporation of the Permanent Gases in a Vacuum; the Limit to the Use of the Hydrogen Thermometer; and the Temperature of Liquid Hydrogen.** By S. WROBLEWSKI (*Compt. rend.*, **100**, 979—982).—The author has shown that the equation which expresses the relation between the temperature and the electromotive force of a thermopile consisting of copper and German silver, for temperatures between  $+100^{\circ}$  and  $-130^{\circ}$ , also expresses the same relation between  $+100^{\circ}$  and  $-193^{\circ}$ , and may fairly be assumed to hold good at still lower temperatures. Determinations of low temperatures by means of this thermopile agree perfectly with those made with a hydrogen thermometer down to  $-193^{\circ}$ , but below this point the temperatures given by the hydrogen thermometer are always lower than those determined by the pile, and the difference is greater the lower the temperature. These facts indicate that below  $-193^{\circ}$  hydrogen no longer obeys Gay-Lussac's law, but contracts more rapidly, and the hydrogen thermometer is consequently valueless for the determination of very low temperatures. It follows that the low temperatures given in former papers as the boiling points of liquefied gases, are in many cases several degrees too low. The following table gives the relation between the tension and the temperature (as determined by the thermopile) of three gases:—

Oxygen.	Nitrogen.	Carbonic oxide.
740 mm. — $181.5^{\circ}$	740 mm. — $193^{\circ}$	735 mm. — $190^{\circ}$
160 „ — $190$	120 „ — $201$	160 „ — $197.5$
140 „ — $190.05$	100 „ — $201.25$	140 „ — $198.4$
100 „ — $190.5$	80 „ — $201.7$	120 „ — $198.5$
90 „ — $190.8$	70 „ — $202.5$	112 „ — $198.75$
80 „ — $191.98$	60 „ — $204$	100 „ — $198.83$
71 „ — $192.71$	42 „ — $206$	60 „ — $201.5$
60 „ — $194.4$	— „ —	40 „ — $201.6$
50 „ — $196.2$		
40 „ — $197.7$		
30 „ — $198.7$		
20 „ — $200.4$		

In the original paper, the table of values for oxygen is more

extensive, and gives the relation for every 2 or 3 mm. It will be seen that when these liquefied gases are evaporated in a vacuum, the minimum temperatures obtained are only a few degrees below  $-200^{\circ}$ . Air does not behave as a simple gas, but as a mixture the constituents of which obey different laws of liquefaction.

When hydrogen is compressed at 180–190 atmos., and cooled by means of nitrogen boiling in a vacuum, and the pressure is suddenly released, a grey cloud forms in the apparatus, but the colour of this cloud could not be definitely ascertained. The thermopile when placed in the interior of the tube showed a temperature of 208–211° when the cloud formed, but how closely this approximates to the true boiling point of hydrogen has still to be determined. C. H. B.

**Dissociation of Nitrogen Peroxide.** By E. and L. NATANSON (*Ann. Phys. Chem.* [2], **24**, 454–467).—After alluding to the various theories propounded to explain the dissociation of gases and the insufficiency of the experimental data, the authors propose to determine the constitution of nitrogen peroxide at various temperatures by determination of the relation between the specific heats at constant pressure and constant temperature, namely, the function ( $k$ ). The investigation was based upon the dust-figure method of Kundt, and the formula given by him  $k = 1.4053 \left( \frac{l}{l'} \right)^2 \frac{d}{d'} \frac{1 + \alpha t}{1 + \alpha t'}$ , in which  $l$ ,  $d$ , and  $t$  are the half wave-lengths, density and temperature of the gas examined,  $l'$ ,  $d'$ , and  $t'$  the same for air. The nitrogen peroxide was prepared by the ordinary process, especial attention being given to the elimination of all traces of moisture from the lead nitrate and the vessels used. The density at the various temperatures was estimated by a manometric method, the vapour being introduced into an exhausted vessel, which was then connected with a manometer; this process, which is given in detail in the original paper, presents considerable advantages over V. Meyer's method in investigations on the dissociation of gases. As a result of the experiments, it follows that the function  $k$  for nitrogen peroxide diminishes with increase of pressure; whereas the reverse has been shown by Wüllner to be the case for carbonic anhydride, nitrous oxide, ammonia, and ethylene. The smallest value found, 1.17 at  $15^{\circ}$ , is approximately equal to that of pent- or hex-atomic molecules, whilst the largest value, 1.27 at  $57^{\circ}$ , is equal to that for triatomic molecules. This fact, taken in connection with the direction of the alteration of the value for  $k$ , presents a further proof that the variation of density of nitrogen peroxide arises from the dissociation of a more into a less complex molecule. Nitrogen peroxide is not then an abnormal exception to Gay-Lussac's law.

V. H. V.

**Tension of Aqueous Vapour of Salt Solutions.** By G. TAMMANN (*Ann. Phys. Chem.* [2], **24**, 523–569).—In this paper an attempt is made to determine the molecular weight of substances in the solid state, by means of the diminution of the tension of aqueous vapour which they produce when dissolved in water. Several years ago, Wüllner established by his experiments that this diminution,

under the same conditions of temperature, was directly proportional to the quantity of dissolved salt. On the other hand, Raoult found that the lowering of the point of congelation in degrees Centigrade is equal to the diminution of tension of aqueous vapour in millimeters divided by the number 7.6 (Abstr., 1879, 4). From the numbers obtained by these observers, the author calculates the relative molecular

*tension diminution* by means of the formula  $\frac{T-T_1}{T_m} M \times 1000$ , in

which  $T$  is the tension of aqueous vapour at the temperature of observation,  $T-T_1$  the tension diminution,  $m$  the quantity of salt dissolved in 100 parts of water, and  $M$  the molecular weight of the salt.

But as the results are far from satisfactory, the author proceeds—(i) to investigate the tension diminution as a function of the temperature and concentration of the solution, and (ii) to demonstrate the probability that an equal number of molecules of salts of analogous constitution produce an equal diminution of vapour-tension of their solution. The method of investigation consists in outline in placing the solution to be examined in one limb of a syphon barometer, and sealing off that limb when the superincumbent space is filled with the vapour of the solution. Five such syphon barometers were used, of which four contained the salt solutions, and the fifth, water. These were all connected with a flask, in which the pressure was determined by a manometer; they were all heated in a water-bath, kept at constant temperature. The necessary corrections and the effect of the various errors of observation are discussed in detail. The observations made at different temperatures with the more common salts of potassium, sodium, lithium, and ammonium, the chlorides of the alkaline earths and magnesium, and of the sulphates of the iron-group, zinc and copper, are given in a series of tables.

Firstly, as regards Wüllner's generalisation that the *tension diminution* is proportional to the quantity of salt dissolved, this is found to hold good only for the sulphates of sodium, ammonium, and magnesium, barium chloride and ammonium bromide; of the other salts examined, some show an increase of relative tension diminution with increase in the quantity of salt dissolved; others, a reverse result; whilst others again show at first an increase, then a decrease. As a result, the following generalisation is propounded; the tension diminution of aqueous vapour by the solution of salts of analogous constitution is inversely proportional to the molecular weight. This is exemplified by the sulphates of various metals and the halogen derivatives of the alkaline earths.

Formula.	Molecular weight.	Relative molecular tension diminution, $\frac{T-T_1}{T_m} \times 1000 \times M$ .
$\text{NiSO}_4 + 6\text{H}_2\text{O}$ .....	263	132
$\text{CoSO}_4 + 6\text{H}_2\text{O}$ .....	263	121
$\text{ZnSO}_4 + 6\text{H}_2\text{O}$ .....	269	122
$\text{MnSO}_4 + 6\text{H}_2\text{O}$ .....	259	109
$\text{MgSO}_4 + 6\text{H}_2\text{O}$ .....	228	143

Formula.	Molecular weight.	Relative molecular tension diminution, $\frac{T-T_1}{T_m} \times 1000 \times M.$
$\text{SrCl}_2 + 6\text{H}_2\text{O}$ .....	266.4	406
$\text{CaCl}_2 + 6\text{H}_2\text{O}$ .....	218.9	422
$\text{MgCl}_2 + 6\text{H}_2\text{O}$ .....	202.9	460
$\text{SrBr}_2 + 6\text{H}_2\text{O}$ .....	355.4	450
$\text{CaBr}_2 + 6\text{H}_2\text{O}$ .....	307.5	513
$\text{MgBr}_2 + 6\text{H}_2\text{O}$ .....	291.9	504

As an application of this method, the instance of beryllium sulphate is given; were the composition of the salt expressible by the formula  $\text{Be}_2(\text{SO}_4)_3 + 12\text{H}_2\text{O}$ , its relative molecular tension diminution should be equal to that of aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$ , but that of the former is 425; of the latter, 299. The molecular tension diminution of beryllium sulphate, if expressed by the formula  $\text{BeSO}_4 + 4\text{H}_2\text{O}$ , is 141, and thus equal to that of magnesium sulphate,  $\text{MgSO}_4 + 6\text{H}_2\text{O} = 143$ ; the formula of beryllium oxide is thus  $\text{BeO}$ . The above generalisation is in accordance with the observations of Kùdorff and De Coppel, who show that salts of analogous constitution lower the point of congelation to an equal degree.

Another relation is brought out by the author's results, namely, if the ratio  $\frac{T-T_1}{T_m}$  decreases with rise of temperature, the salt dissolves in water with evolution of heat, and conversely if  $\frac{T-T_1}{T_m}$  increases, the salt dissolves with absorption of heat.

In cases of salts which possess no water of crystallisation, the tension of vapour from water, and from the salt solution under the same conditions of temperature, is expressible by the ratio  $T - T' = N \frac{mv^2}{2} = N' \frac{m'v'^2}{2}$ , in which  $N$  and  $N'$  are the number of water molecules within a given space,  $m$  and  $m'$  their masses, and  $v$  and  $v'$  their velocities. If water vapour behaves as an ideal gas, then  $\frac{1}{2}mv^2 = \frac{1}{2}m'v'^2$ , and  $\frac{T}{T'} = \frac{N}{N'}$ , as also  $\frac{T-T_1}{T-T_2} = \frac{N-N_1}{N-N_2}$ . The tension diminution will thus be independent of the number of molecules of aqueous vapour resulting from the solution. But it is clear that the greater the concentration of the salt solution, the more effectually will the water molecules be retained from vaporisation, so that in such cases the number of water molecules retained is directly proportional to the quantity of salt dissolved. The following proportions then hold good:  $\frac{N-N_1}{N-N_2}$  or  $\frac{T-T_1}{T-T_2} = \frac{m_1}{m_2}$ , where  $m_1$  and  $m_2$  are the number of salt molecules in 100 parts of water; or to put this relation in another form, the quotients of relative tension diminution by relative volume will be equal. This generalisation is exemplified in the cases of potassium chromate and the halogen salts of the alkali metals. As regards salts with water of crystallisation, one cannot decide whether the decrease of tension diminution is conditioned by the formation of

double molecules, or by hydrates containing a less proportion of water.

V. H. V.

**On the Nature of Solution.** By W. L. GOODWIN (*Trans. Roy. Soc. Edin.*, 30, 597—618).—Two theories have been propounded to explain the phenomenon of solution; the one based on the assumption of a chemical action between the solvent and the substance dissolved, the other on a mechanical interpenetration of the solid molecules into the molecular interstices of the liquid. It is probable that solution is to be explained in part by both these theories; for in some cases the phenomenon is analogous to the diffusion of gases, whilst in others a chemical action is required to break up the congeries of the molecules. In this paper, the solubility of chlorine in water and saline solutions is more particularly studied.

The solubility of chlorine in water increases with a rise of temperature until a maximum is reached at 10—11°; from this point the solubility decreases. The result is to be explained by the solution of the solid chlorine hydrate, which is subsequently decomposed, thus resolving the phenomenon to the simple case of the solubility of gas in a liquid. Similar results were obtained with the chlorides of the alkali metals, although the presence of these salts induces the decomposition of the chlorine hydrate at a somewhat lower temperature than pure water; whilst the chlorides of magnesium, calcium, iron, cobalt, and strontium prevent the formation of the chlorine hydrate. In these cases, however, the solubility of the chlorine seems to follow the same general course; for the curves representing the solubility as a function of the temperature are flat at the maxima points, while from them the descent is very gradual. The occurrence of maxima points in the case of these salts can be explained as a result of two opposing forces, namely, the solubility of the chlorine in the water, not chemically combined with the salt, and the attraction of the chloride for the water, which thus determines the amount of uncombined water. As the temperature falls, the amount of free water decreases, whilst the coefficient of absorption increases at a quicker rate; therefore, on the whole, the solubility increases as the temperature falls.

But in all cases examined there is a general tendency towards coincidence at high temperatures. The curves for solutions containing two chlorides, each of which permits the formation of chlorine hydrate, follows the mean course between those of the chlorides taken separately, although this is not the case when only one or both prevent the formation of the hydrate.

The solubility of chlorine in water is increased by the presence of hydrochloric acid, and of lithium and possibly of strontium chlorides.

As a general result, it may be stated that the presence of chlorides affects the solubility of chlorine, *chemically* at low, but *mechanically* at high temperatures. The explanation of the phenomena presented is thus based upon both of the theories enunciated above.

V. H. V.

**Solubility of Mixtures of Salts.** By F. RÜDORFF (*Ber.*, 18, 1159—1162; compare this Journal, 1873, 1101).—From the experi-



ments described the author concludes that those salts which are isomorphous, or which form together double salts, displace one another from their solutions, whilst those salts which do not crystallise together do not displace each other. Several examples are given, all of which confirm this view. N. H. M.

**Attraction between Dissolved Substances and Solids Immersed in the Solutions.** By J. THOULET (*Compt. rend.*, 100, 1002—1005).—The author has previously shown (this vol., p. 476) that an attraction is exerted between a dissolved solid and a solid immersed in the solution. Further experiments with powdered quartz and a solution of barium chloride show that this attraction is exerted instantaneously, and that other conditions being equal, the attraction is directly proportional to the surface of the immersed solid.

C. H. B.

**Capillary Constants of Certain Aqueous and Alcoholic Solutions.** By J. TRAUBE (*J. pr. Chem.* [2], 31, 177—219).—The apparatus employed is described, and a previous paper referred to (this vol., p. 116). The conclusions drawn are as follows:—

The specific cohesion of mixtures of two liquids does not necessarily lie between the values shown by the component liquids, but may be lower than either.

The cohesion of a saturated solution of an organic liquid generally differs but slightly from that of the dissolved substance itself; thus a saturated solution of aniline shows  $\alpha = 4.577$ , whilst with aniline  $\alpha = 4.311$ .

In the case of aqueous solutions of salts, the rise of the liquid is almost proportional to the specific gravity, irrespective of the nature of the salts. This, however, is not quite true, increased strength of most solutions is accompanied by slightly increased capillary action, whilst with some few a slight decrease is noticed. In this respect the latter solutions resemble, in a degree, the aqueous solutions of certain common organic liquids which show a rapidly decreasing action with increasing strength; from this the author concludes, and seems to lay stress on the conclusion, that no distinction is to be drawn between the behaviour of aqueous solutions of inorganic salts and organic substances or liquids.

The principal result obtained from the study of solutions of salts in dilute alcohol is, that for any given salt a particular strength of dilute alcohol may be found, such that when used as a solvent, the capillary height varies inversely with the specific gravity of the solution. The strength of alcohol required for the members of a particular series of salts is almost the same, but differs from that required by other series of salts. H. B.

**Capillary Constants of Liquids and Cohesion of Solids.** By A. BARTOLI (*Gazzetta*, 14, 553—562).—As a deduction from the experiments of Frankenheim, Quincke, and others, on the capillary constants of liquids, the author enunciated the following generalisation: the quotient  $\frac{a^2}{cd}$  (in which  $a^2$  is the constant of capillarity for a

cylinder of 1 mm. radius,  $c$  the specific heat, and  $d$  the sp. gr.), is practically constant for liquids containing carbon, hydrogen, oxygen, and sulphur, but is slightly diminished if the halogen elements are present. As examples, the values for  $\frac{a^2}{cd}$  are given for the paraffin-hydrocarbons separated from Pennsylvania petroleum, also for aqueous solutions of glycerol of various concentrations.

Cantoni and Vogel have observed that the heat of expansion (*i.e.*, the number of heat-units required to produce a given expansion) is, in the case of metals, proportional to the coefficient of elasticity, whilst Carnelley has established a relation between the coefficient expansion and the freezing point. In this paper, it is shown that  $\beta \frac{P^4}{D^4}$  and  $\beta \left(\frac{P}{D}\right)^{\frac{2}{3}} P k^2$  are constants, in which  $P$  is the atomic weight,  $k$  the coefficient of expansion,  $D$  the sp. gr., and  $\beta$  the cohesion referred to unit of superficies.

V. H. V.

**Capillary Gas Absorption.** By R. W. BUNSEN (*Ann. Phys. Chem.* [2], 24, 321—347).—In a former paper, the author has shown that glass surfaces absorb carbonic anhydride, and that the velocity of condensation decreases with time of contact and fall of temperature, but increases with rise of temperature (*Abstr.*, 1884, 146, compare Bottomley, this vol., p. 447). As silicates of composition approximating to that of glass retain moisture even at high temperatures, this phenomenon is here more particularly studied, as tending to throw light upon the former observations. Determinations were made of the thickness of a water layer retained by glass thread of known superficies, when the glass was heated at a constant temperature in a continuous current of dry air. Experiments showed that the evaporation of the capillary water layer proceeded slowly until a zero point was reached; on raising the temperature, the evaporation recommenced up to the zero point corresponding to that temperature. Thus, glass thread presenting a superficies of 2.11 square metres retained at 23° 22.3 mgrms. of water, at 215° 11.6 mgrms., and only at a temperature of 503° was no water eliminated. The glass retaining the water by capillary attraction was then submitted to a current of dry carbonic anhydride, and it was found that 1 c.c. of water, under such conditions, can absorb as much as 48,700 c.c. of carbonic anhydride under standard conditions, the percentage composition of the resultant material may be expressed thus:—

Carbonic anhydride.....	80.9
Water .....	19.1

It is not, however, easy to understand in what manner the carbonic anhydride is associated with the water, whether in the liquid or solid state, or in chemical combination as a hydrate. No condensation of carbonic anhydride occurs when the surface of the glass is perfectly free from moisture, and the carbonic anhydride can be evaporated off by a current of oxygen. The phenomenon of gas condensa-

tion, as observed by the author, but attributed by other writers to errors of observation, is thus a necessary consequence of the phenomenon of capillary gas absorption. The retention of water by glass is in all probability the cause of errors in gas analysis, which can only be avoided when the glass apparatus is heated to a high temperature before use.

V. H. V.

**Action of Compressed Carbonic Anhydride on Glass.** By L. PFAUNDLER (*Ann. Phys. Chem.* [2], 24, 493—494).—After alluding to Bunsen's researches on the condensation of carbonic anhydride on glass (Abstr., 1884, 146), the author gives an account of an observation which tends to show that under certain conditions carbonic anhydride can attack glass. When a strong light is projected upon a glass tube filled with compressed carbonic anhydride near its critical point, the surface of the glass above the level of the liquefied gas is found to be corroded as though with hydrofluoric acid. It is thus not improbable that a chemical action, effected within a few minutes under the influence of a strong pressure and intense light, can proceed slowly, under a slight pressure and ordinary daylight. The observations of Bunsen can then be explained, as resulting from chemical action, rather than from interpenetration of the glass by carbonic anhydride, more especially as Bessel Hagen (*Ann. Phys. Chem.* [2], 12, 425—440) has proved that not the slightest trace of hydrogen under the pressure of one atmosphere can penetrate a thick-walled glass tube, even after the interval of a year.

V. H. V.

**Principle of Maximum Work.** By BERTHELOT (*Bull. Soc. Chim.*, 43, 265—272).—The principle of maximum work reduces the phenomena of chemical change to two fundamental data, the one, the heat evolved in the reaction taken by itself, the other, the heat change resulting from the dissociation of the reacting substances. Although it cannot at present be definitely stated that an absorption of heat never results from chemical action, yet such an absorption always results from a decrease of energy, brought about by dissociation of the original substances or their derivatives, or from a change of physical state and specific heat. These phenomena of dissociation, fusion, vaporisation, and in general physical changes result from the temperature required for the chemical action; thus, chemical affinity, in so far as it is measured by the heat disengaged, is expressed by the sum of two terms, the one a constant, or the heat disengaged at 273°, the other variable with the absolute temperature. The latter function of the temperature can only acquire a certain value in cases in which dissociation has commenced, whether of the initially reacting substances or of secondary compounds, such as hydrates, acids, or double salts. Although this condition of dissociation is essential for the production of chemical equilibrium, yet it is further necessary that it should give rise to a cycle of reversible changes, such as the double decomposition between the metallic chlorides, bromides, and iodides. Thus the author has shown that whether potassium bromide reacts with silver chloride, or silver bromide with potassium chloride,

there is equally an evolution of heat (an observation confirmed by Potilitzin, who has proved that bromine can replace, to a certain degree, its equivalent of chlorine in metallic chlorides). These reversible phenomena are due to the production of metallic perbromides and chlorobromides, the existence of which explains the difficulty experienced in the complete displacement of bromine by chlorine. At low temperatures, when the chemical change is not complicated by changes in physical state, the action of bromine on chlorides is always accompanied by an evolution of heat.

V. H. V.

**Impermeability of Glass to Gases.** By A. BARTOLI (*Gazzetta*, **14**, 544—548).—Previous experiments on the permeability of glass to gases has shown that even under pressures of 126 atmos. not even infinitesimal quantities of gases pass through glass. In order to examine this point by a method different from those hitherto adopted, the author sealed up, in two hard glass tubes, bent so as to form three sides of a rectangle, potassium chlorate and manganese peroxide in the one, and zinc with sulphuric acid in the other. One limb each of these glass tubes was covered with gold foil, and immersed in the same vessel containing a solution of sodium sulphate. The gold foil was in circuit with a differential galvanometer. By warming up the other limb to generate hydrogen and oxygen respectively, no difference of potential was observed, even though the pressure in the hydrogen tube varied from 10 to 20 atmos., and in the oxygen tube from 4 to 8 atmos. Other experiments were made with a view of testing whether hydrogen or oxygen generated by the electrolysis of sodium sulphate could penetrate glass; but here again the result was negative. If the hydrogen had diffused through the glass so as to cover the gilded surface with a density of one thirty-four-millionth of a millimetre per square metre surface, or, in weight, of three-billionths of a gram per square metre, it would have been indicated by the galvanometer, as the arrangement was sensitive to a difference of potential of one-millionth of a Daniell.

V. H. V.

**Lecture Experiment.** By F. RÜDORFF (*Ber.*, **18**, 1162).—Displacement of a salt from its solution by another salt (comp. p. 865) can be shown by adding a little finely powdered ammonium sulphate to a saturated solution of ammonium copper sulphate, and shaking well for a minute or two. After a few moments the solution loses its colour more or less completely, and is in any case much fainter in colour than the original solution.

N. H. M.

## Inorganic Chemistry.

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**Molecular Weight of Fluid Water.** By J. THOMSEN (*Ber.*, 18, 1088).

**Oxidation of Iodine during Nitrification.** By A. MÜNTZ (*Compt. rend.*, 100, 1136—1138).—When potassium iodide is added to a solution of a nitrogenous organic compound undergoing nitrification by natural fermentation under suitable conditions, the iodide is partly oxidised to iodate, which can be separated as barium iodate. The iodate existing in the deposits of sodium nitrate in South America has probably been formed from iodide in a similar manner. The organisms which will reduce nitrate when out of contact with air, will, under the same conditions, reduce iodates. C. H. B.

**The Basicity of Hyposulphuric Acid.** By H. TREY (*J. pr. Chem.* [2], 31, 223—233).—Ostwald has shown that the solvent action of a monobasic acid is increased by the addition of its neutral salts, whilst that of a bibasic acid is thereby decreased. It is now shown that the action of dilute hydrochloric and of sulphuric acids upon methyl acetate is respectively increased and decreased by the addition of the neutral salts of these two acids; the amount of methyl acetate decomposed was measured by the amount of baryta-water required to saturate the acetic acid liberated. The action of hyposulphuric acid in dilute solution is, like that of hydrochloric acid, increased by the addition of the neutral sodium salt, and hence hyposulphuric acid is, as supposed by Kolbe, a monobasic acid,  $\text{HSO}_3$  or  $\text{SO}_2\text{-OH}$ , in which the sulphur-atom is pentavalent. H. B.

**Tellurous Anhydride and its Compounds.** By D. KLEIN and J. MOREL (*Compt. rend.*, 100, 1140—1143).—Tellurous anhydride obtained in quadratic octohedra in the wet way, has a sp. gr. of 5.67 (uncorr.) at  $0^\circ$ . The anhydride obtained in long white rhombic needles by fusion has a sp. gr. of 5.91 (uncorr.) at  $0^\circ$ , whilst the sp. gr. of the variety obtained by strongly heating the basic nitrate is 5.68 (uncorr.) at  $0^\circ$ .

The basic nitrate,  $8\text{TeO}_2 \cdot 2\text{N}_2\text{O}_5 + 3\text{H}_2\text{O}$ , previously described, forms rhombic prisms, with the angles  $m:m$ ,  $99.18$ ;  $a':a'$ ,  $74.34$ ;  $m:h'$ ,  $139.42$ ;  $a':h'$ ,  $122.14$ ;  $m:a'$ ,  $114.12$ ;  $g^3:h'$ ,  $122.18$ ;  $g^2:h'$ ,  $109.32$ .

*Potassium hexatellurite*,  $\text{K}_2\text{O} \cdot 6\text{TeO}_2 + 2\text{H}_2\text{O}$ , is obtained by the action of oxalic acid on potassium tellurite. It forms a light white amorphous powder, not decomposed by boiling water, in which it is only slightly soluble. It melts at a dull red heat with intumescence, and loses water.

A concentrated solution of ordinary phosphoric acid dissolves tellurous anhydride, and on spontaneous evaporation the solution deposits a white light amorphous powder, which cannot be purified. Water or alcohol removes phosphoric acid and leaves tellurous acid or tellurous anhydride according to the conditions. The action of

citric and tartaric acids on potassium, sodium, and lithium tellurites yields double salts which seem to be analogous to tartar emetic.

C. H. B.

**Change of Arsenious Oxide from the Amorphous to the Crystalline Condition.** By C. WINKLER (*J. pr. Chem.* [2], **31**, 247—261).—Pieces of vitreous oxide retain their transparency any length of time in dry air, hydrogen, or carbonic anhydride; whilst in moist air opalescence begins in 3 to 7 days, and in 15 months the change is complete, 0.3315 per cent. of moisture being at the same time absorbed; this cannot be completely removed at  $110^{\circ}$ . The sp. gr. of the vitreous oxide is 3.6815, of the opaque oxide 3.6461; petroleum was used in the determination. The solubility and rate of solution of the two varieties in water is very different; 100 parts of water dissolve of—

	One hour.	Six hours.	Three weeks.
Vitreous oxide.....	1.589	3.666	3.713
Crystalline oxide....	0.023	0.353	1.776

The vitreous oxide is, however, gradually converted into the crystalline oxide, small crystals being deposited on the sides of the tubes in 12 hours. The solubilities of the two varieties are therefore about 3.7 and 1.7 in 100 parts of cold water, whilst in the first hour 70 times as much of the vitreous oxide is dissolved as of the crystalline oxide; these data explain the change in the vitreous oxide brought about by the presence of a mere trace of water.

H. B.

**Preparation of Arsenic Acid and Existence of Compounds of Arsenic and Arsenious Acids.** By A. JOLY (*Compt. rend.*, **100**, 1221—1224).—If 100 grams of finely-powdered arsenious oxide are mixed with 25—30 c.c. of ordinary nitric acid, there is very little action in the cold. On heating gently, the reaction commences, but after a little time the mass becomes solid, and is found to consist of small nacreous crystals. If this product is heated to expel excess of acid, and then dissolved in boiling water, the solution on cooling deposits octahedral crystals of arsenious oxide, and afterwards acicular crystals of the composition  $2\text{As}_2\text{O}_5, 3\text{As}_2\text{O}_3 + \text{H}_2\text{O}$ , which separate from a mother-liquor containing an excess of arsenic acid. When these crystals are moistened with water, they decompose with separation of octohedra of arsenious oxide. These facts explain why nitric acid of not higher sp. gr. than 1.35 should be used in the industrial preparation of arsenic acid.

If the above operation is so modified that a very large proportion of arsenious oxide remains unoxidised, the double compound which separates has the composition  $\text{As}_2\text{O}_5, 2\text{As}_2\text{O}_3 + \text{H}_2\text{O}$ . In presence of a large excess of arsenic acid the compound  $\text{As}_2\text{O}_5, \text{As}_2\text{O}_3 + \text{H}_2\text{O}$  separates in slender needles. In most cases, however, a mixture of the three double compounds is obtained. The degree of hydration of these compounds could not be definitely ascertained.

All the compounds are dissolved and more or less completely decomposed by water, and the solution when concentrated deposits arsenious oxide and then one or other of the double compounds, whilst

the mother-liquor contains a large quantity of arsenic acid. In alkaline solutions, decomposition seems to be complete, and this fact is doubtless closely connected with the well-known fact that arsenious oxide is much more easily oxidised in alkaline than in neutral or acid solution.

C. H. B.

**Apparent Volatilisation of Silicon at 440°.** By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, 100, 1220—1221).—Troost and Hautefeuille found that when vapour of aluminium chloride is passed over aluminium heated at 1300°, the cool part of the tube contains globules of aluminium, probably formed by the successive formation and decomposition of an aluminium subchloride. The authors find that when vapour of aluminium chloride is passed over aluminium heated at 440° only in a glass tube, a deposit is formed of an amorphous substance, which consists mainly of silicon with small quantities of iron and aluminium. It would seem, therefore, that silicon is retained by aluminium heated at 1300°, but is given up when the metal is heated at a temperature much below its softening point.

C. H. B.

**Phosphates.** By H. GRANDEAU (*Compt. rend.*, 100, 1134—1135).—The author has prepared a large number of phosphates by the action of potassium sulphate on different phosphates at high temperatures (Abstr., 1883, 151), but no descriptions or details are given.

C. H. B.

**Limit to the Combination of Magnesium and Potassium Hydrogen Carbonates.** By R. ENGEL (*Compt. rend.*, 100, 1224—1226).—The author has previously shown that potassium hydrogen carbonate decomposes magnesium hydrogen carbonate with formation of the double compound,  $\text{MgCO}_3 \cdot \text{KHCO}_3 + 4\text{H}_2\text{O}$ . This salt can also be formed, with considerable development of heat, by the direct action of potassium hydrogen carbonate on normal magnesium carbonate.

The author has investigated the conditions of equilibrium when the two bicarbonates react (1) in presence of carbonic anhydride at different pressures, and (2) in presence of a different proportion of one of the salts. The proportion of the double salt formed diminishes as the pressure of the carbonic anhydride increases, but increases with the proportion of potassium hydrogen carbonate, the reaction tending to a maximum in both cases. The results can be represented by a formula which gives the amounts of sulphuric acid neutralised by the unaltered potassium hydrogen carbonate and magnesium carbonate respectively.

C. H. B.

**Copper Oxides.** By JOANNIS (*Compt. rend.*, 100, 999—1001).—When an oxide having the composition  $\text{Cu}_3\text{O}_2$ , obtained by fusing cupric oxide, is dissolved in a mixture of hydrochloric acid and ammonium iodide, the development of heat is the same as that which accompanies the solution of a mixture of cupric and cuprous oxides, having the same percentage composition. The mixed oxides were

previously heated separately to the same temperature as the fused oxide. It follows that the substance having the composition  $\text{Cu}_3\text{O}_2$  is really a mixture of cupric and cuprous oxides, and this also holds good in the case of other oxides, said to be intermediate between cupric oxide and cuprous oxide (comp. this vol., pp. 22 and 23).

C. H. B.

#### Ammonio-cupric Sulphate and a Basic Cupric Sulphate.

By G. ANDRÉ (*Compt. rend.*, **100**, 1138—1140).—If a rapid current of ammonia gas is passed for a long time into a well-cooled saturated solution of cupric sulphate, the whole of the copper is precipitated in the form of the well-known ammonio-cupric sulphate,



which separates in long acicular crystals.

When this ammonio-cupric sulphate is heated with 10 times its weight of water in sealed tubes at  $200^\circ$  for five hours, the sides of the tube become coated with black cupric oxide. Cupric oxide also separates in small quantity when a solution of ammonio-cupric sulphate is evaporated in presence of air. The composition of the green precipitate which forms in the solution after a time does not seem to be constant.

If an aqueous solution of ammonio-cupric sulphate is gently heated with metallic copper in a flask with a drawn-out neck, the slight deposit of cupric oxide which forms at first soon changes to apple-green, and if the clear liquid is decanted and heated with fresh copper, the green substance continues to form. It has the composition of  $7\text{CuO}, 2\text{SO}_3, 7\text{H}_2\text{O}$ , when dried at  $100^\circ$ . This green basic sulphate can be obtained in several other ways, namely, by heating with ammonium sulphate solution the blue basic sulphate obtained by adding a small quantity of ammonia to a solution of cupric sulphate; by heating the blue basic salt,  $4\text{CuO}, \text{SO}_3, 16\text{H}_2\text{O}$  (obtained by saturating ammonium sulphate solution with cupric oxide, and cooling the liquid), with ammonium sulphate solution; by heating a saturated solution of cupric oxide in ammonium sulphate solution with excess of water in sealed tubes at  $200^\circ$ ; by mixing equal vols. of a saturated solution of cupric sulphate with a saturated solution of ammonio-cupric sulphate, and allowing to stand, or heating in sealed tubes at  $150^\circ$ . The basic sulphate is not decomposed by cold water, but when heated with ammonium sulphate solution it partially dissolves to a blue solution.

C. H. B.

**Action of Aluminium on Aluminium Chloride.** By C. FRIEDEL and L. ROUX (*Compt. rend.*, **100**, 1191—1193).—When vapour of aluminium chloride is passed over metallic aluminium heated just to fusion a brownish-grey substance is formed, which contains aluminium, chlorine, and silicon. If aluminium and aluminium chloride are heated at  $300^\circ$  in sealed tubes filled with carbonic anhydride, there is no appreciable action, but at  $360^\circ$  (in the vapour of mercury) the aluminium is slightly attacked, and large crystals of pure aluminium chloride condense on the cool upper part of the tube. When the tubes are heated in the vapour of sulphur, the



aluminium is strongly attacked, and a greyish substance with a somewhat metallic appearance is deposited on the sides of the tube. This substance decomposes water with evolution of hydrogen, and contains silicon, chlorine, and aluminium. A similar substance is obtained by bringing aluminium and bromine in the ratio  $\text{Al}:\text{Br}_2$  in contact in sealed tubes, and heating the tubes in sulphur vapour after all action has ceased.

When silicon chloride vapour and hydrogen are passed over aluminium heated to dull redness, aluminium chloride and silicon are formed.

C. H. B.

**Aluminium Oxychlorides.** By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, **100**, 1219—1220).—When aluminium is heated below incipient redness in a mixture of oxygen and vapour of aluminium chloride, it takes fire, and if the source of heat is withdrawn, combustion continues with production of white bulky flakes which contain oxygen, chlorine, and aluminium, the proportion of oxygen being higher the higher the temperature at which combustion takes place. The composition of the products obtained points to the existence of oxychlorides containing from 2 to 8 equivalents of alumina to each equivalent of aluminium chloride. The combustion of aluminium in a mixture of chlorine and oxygen also yields oxychlorides containing not less than 5 equivalents of oxygen for each equivalent of chlorine.

These oxychlorides are white crystalline substances which act on polarised light with an energy which increases with the proportion of oxygen. They are decomposed by water, and dissolve in very dilute acids and alkalis, the solubility increasing with the proportion of chlorine.

C. H. B.

**Cobaltammonium Compounds. Sulphatopurpureocobalt Salts.** By S. M. JÖRGENSEN (*J. pr. Chem.* [2], **31**, 262—272).—So far only purpureocobalt salts of monobasic acids have been obtained; an acid sulphate has, however, been described and examined with various results by Gibbs and Genth. This salt has now been re-examined, and its mode of preparation carefully described; it forms violet-red plates. Its constitution is determined as follows:—The salt,  $\text{Co}_2(10\text{NH}_3, \text{SO}_4)_2, 2\text{SO}_4\text{H} + 4\text{H}_2\text{O}$ , has a strongly acid reaction and alcohol added to its solution throws down a neutral salt,  $\text{Co}_210\text{NH}_3, 3\text{SO}_4$ ; hence the original substance is an acid salt. The neutral salt treated with sodium platinochloride, or the acid salt treated with hydrogen platinochloride, yields a double salt,  $\text{Co}_210\text{NH}_3(\text{SO}_4)_2, \text{PtCl}_6$ , and hence the base is bibasic and not quadribasic, in other words, two of the sulphur-groups belong to the basic radicle. This is further proved by the formation of the nitrate,  $\text{Co}_210\text{NH}_3(\text{SO}_4)_2, 2\text{NO}_3$ , by the addition of ammonium nitrate to the acid sulphate, and by the fact that barium chloride does not precipitate the solution of this nitrate. The acid sulphate boiled with dilute hydrochloric acid is completely converted into chloropurpureo-chloride, and with dilute ammonia it is converted into a roseo-salt, hence it is acid sulphatopurpureo-sulphate.

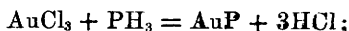
The preparation and reactions of this and the allied salts are described, namely :—Normal sulphate,  $(\text{SO}_4)_2(\text{Co}_2, 10\text{NH}_3)\text{SO}_4, \text{H}_2\text{O}$  ; nitrate,  $(\text{SO}_4)_2(\text{Co}_2, 10\text{NH}_3), 2\text{NO}_3$  ; bromide,  $(\text{SO}_4)_2(\text{Co}_2, 10\text{NH}_3)\text{Br}_2$  ; platinumchloride, sulphate,  $(\text{SO}_4)_2(\text{Co}_2, 10\text{NH}_3)\text{PtCl}_6, 2\text{H}_2\text{O}$ . H. B.

**Hydrochloride of Chromous Chloride.** By RECOURA (*Compt. rend.*, 100, 1227—1228).—When a current of dry hydrogen chloride carefully freed from oxygen is passed for some time into a well-cooled solution of chromous chloride, a more or less deep blue precipitate is formed, which eventually changes to bluish-white. The final product is washed with benzene free from air, and dried in a current of hydrogen chloride free from oxygen. It has the composition  $2\text{HCl}, 3\text{CrCl}_2, 13\text{H}_2\text{O}$ . It dissociates in the mother-liquor at  $20^\circ$  with evolution of hydrogen chloride. C. H. B.

**New Complex Inorganic Acids.** By W. GIBBS (*Ber.*, 18, 1089).

**Bismuth Antimoniates.** By A. CAVAZZI (*Gazzetta*, 15, 37—40).—*Bismuthyl antimonate*,  $(\text{BiO})\text{SbO}_3\text{Aq}$ , can be prepared as an amorphous precipitate by adding a concentrated solution of potassium antimonate to a dilute solution of bismuth ammonium citrate. It is insoluble in water, soluble in hydrochloric acid ; it is fusible only at high temperatures. If the above change is conducted in the presence of an excess of ammonia a basic bismuth antimonate,  $(2\text{BiO})_3\text{SbO}_4, \text{H}_2\text{O}$ , is produced as a gelatinous precipitate, insoluble in water, soluble in hydrochloric acid. V. H. V.

**Action of Phosphine on Auric Chloride.** By A. CAVAZZI (*Gazzetta*, 15, 40—44).—If hydrogen phosphide is passed into a solution of auric chloride in ether or alcohol, a black precipitate of gold phosphide is formed in accordance with the equation—



it is decomposed in the presence of air, producing phosphoric acid ; when boiled with water or alkalis, it yields hydrogen, phosphine and phosphoric acid, together with metallic gold. But if phosphine is passed into an aqueous solution of auric chloride, phosphorous and phosphoric acids are produced along with metallic gold, a result due to the decomposition by the water of the gold phosphide initially formed. V. H. V.

**Purple of Cassius.** By H. DEBRAY (*Compt. rend.*, 100, 1035—1037).—A note on a recent paper by Müller (this vol., p. 352).

C. H. B.

## Mineralogical Chemistry.

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**Occurrence of Native Mercury in the Alluvium in Louisiana.** By E. WILKINSON (*Amer. J. Sci.*, **29**, 280—281).—Native mercury has been recently discovered in a locality where its presence has hitherto been unsuspected. At Cedar Grove Plantation, Louisiana, native mercury occurs disseminated through the alluvial soil. It seems thoroughly mixed with the soil, and is found for a distance of 1,200 feet. Several specimens of the soil, 1 to 5 feet below the surface, gave a mean percentage of mercury of 0.002934.

B. H. B.

**Chemical Composition of Coal.** By P. F. REINSCH (*Dingl. polyt. J.*, **256**, 224—226).—The author concludes that by means of alkaline solvents it is possible to isolate from coal, substances which are quite amorphous, do not exhibit signs of organic structure, possess dyeing properties, and are characterised by their resistance to concentrated mineral acids and atmospheric influences. He is of opinion that coal is composed of two substances, which are distinguished by the difference in their behaviour with alkaline solutions.

D. B.

**Non-volcanic Origin of Boric Acid.** By DIEULAFAIT (*Compt. rend.*, **100**, 1017—1019).—The water which circulates in the upper part of the sand in the district of Ouargla contains about 2.2 per cent. of dissolved salts. Boric acid could be readily detected in 0.5 gram of the residue, strontium and lithium being also easily recognised. The saline matter has in all probability been derived originally from sea-water, and the presence of boric acid affords further proof that this substance is not always of volcanic origin.

C. H. B.

**Origin of Boric Acid.** By DIEULAFAIT (*Compt. rend.*, **100**, 1240—1243).—The springs at Montecatini, between Florence and Pistoja, in a district of ophiolitic and serpentinous rocks, contain large quantities of lithium, which can be recognised spectroscopically in one drop of the water, and are also very rich in strontium and boric acid. Since there are no visible manifestations of volcanic action in the district, it is evident that the boric acid must be derived from the tertiary deposits in the district, and therefore had originally an aqueous origin, and is derived from the waters of ancient seas.

C. H. B.

**Colemanite.** By A. W. JACKSON (*Amer. J. Sci.*, **29**, 341—342).—The author has given a preliminary notice (*Abstr.*, 1885, 358) of the crystalline form of colemanite. He now publishes an exhaustive monograph on the same subject in Bulletin No. 2 of the California Academy of Sciences. His results show colemanite to be one of the most remarkable of minerals, both in the beauty and perfection of the crystals, and the complexity of their forms. He gives a list of 40 planes which he has identified upon the crystals under examination. The crystals have a perfect cleavage parallel to the clinopinacoid, and the habit varies from medium to short columnar.

The author's results are confirmed by those of v. Rath (this vol., p. 224) and Hiortdahl (this vol., p. 730). B. H. B.

**Distribution of Phosphates in Bohemia.** By J. STOKLASA (*Bied. Centr.*, 1885, 230—232).—In the neighbourhood of Blosdorf, on the freestone, a new phosphatic mineral has been found of the consistency of clay, blue-green, and containing organic matter; after hardening, lustre metallic. Sp. gr. at 17°, 2·5804. i. Composition; ii. Soluble in HCl:—

	P <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .	SO <sub>3</sub> .	K <sub>2</sub> O.	Na <sub>2</sub> O.	MgO.
(i.)	14·702	46·082	0·362	1·634	2·436	0·733
(ii.)	14·702	5·384	0·362	0·504	0·936	0·354
	CaO.	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .	Loss on ignition.		Total.	
	2·154	30·542	2·115		100·76	
	1·871	10·257	—		34·37	

In basaltic tufa near Tetschin, yellow nodules of fatty lustre were found. Sp. gr. at 15°, 2·805. Composition:—

P <sub>2</sub> O <sub>5</sub> .	CO <sub>2</sub> .	SiO <sub>2</sub> .	SO <sub>3</sub> .	Cl.	F.
36·102	3·044	5·316	0·750	trace	trace
CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .	Water and org. matter.		Total.
52·432	0·425	2·000	2·541		100·67

In the basalt of Falkenberg two tufas containing phosphates have been found; the one kind, tabular and yellow-grey, evolved ammonia when heated with soda-lime, and is soluble to the extent of  $\frac{1}{4}$  in hydrochloric acid; the other tufa is globular and more soluble in acid. Composition:—

	Tabular mineral.		Globular form.	
	Soluble in HCl.	Insoluble.	Soluble in HCl.	Insoluble.
P <sub>2</sub> O <sub>5</sub> .....	0·903	1·632	1·110	—
SiO <sub>2</sub> .....	5·322	0·920	6·401	44·121
SO <sub>3</sub> .....	trace	0·363	—	—
K <sub>2</sub> O .....	0·893	0·760	1·352	2·010
Na <sub>2</sub> O .....	1·940	12·243	2·560	0·635
MgO .....	0·543	48·003	0·156	0·213
CaO .....	5·241	—	3·042	0·366
Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .....	16·213	—	17·342	14·215
	29·055	63·921	31·966	61·560

Other tufas containing phosphoric acid have been found, but are not fully described. E. W. P.

**Koninckite, a New Hydrated Phosphate of Iron.** By G. CESÀRO (*Amer. J. Sci.*, **29**, 342).—The author describes a new iron phosphate from Visé, Belgium. It occurs in small globular forms, consisting of transparent radiating needles. The needles have a single perfect cleavage, and belong to the monoclinic system;  $H. = 3.5$ . Sp. gr. 2.3. An analysis gave the following results:—

$P_2O_5$ .	$Fe_2O_3$ .	$Al_2O_3$ .	$H_2O$ .	Total.
34.8	33.9	(4.5)	26.8	100.0

From this the formula  $Fe_2O_3.P_2O_5 + 6H_2O$  is calculated.

Koninckite occurs associated with richellite (see Abstr., 1884, 1102). B. H. B.

**Analysis of Titanic Iron Sand from Brazil.** By J. B. MACKINTOSH (*Amer. J. Sci.*, **29**, 342—343).—The mineral analysed occurs in river or beach sands in small rounded grains, associated with monazite, garnet, tourmaline, quartz, and mica. Sp. gr. 4.2. Analysis gave the following results:—

$TiO_2$ .	$Fe_2O_3$ .	$FeO$ .	$MgO$ .	$SiO_2$ .	Total.
59.20	32.11	4.9	1.73	1.16	99.10

These figures lead to the formula  $3(Fe_2O_3, 3TiO_2) + 2(FeO, TiO_2)$ .

B. H. B.

**Mineralogical Notes.** By W. E. HIDDEN (*Amer. J. Sci.*, **29**, 249—251).—*Phenacite*.—The author has found colourless crystals of phenacite implanted in considerable numbers on quartz, topaz, and microcline from Florissant, El Paso County, Colorado. The phenacites are well polished, transparent, and highly modified.

*Xenotime*.—From the same locality as the phenacite, the author received, along with some bastnaesite, a single tetragonal crystal of 5.1 grams weight. A fragment tested showed the presence of phosphoric acid, iron, lime, and yttria. Its sp. gr. was 4.48. The planes  $P$ ,  $\infty P$ ,  $OP$  were largely developed,  $OP$  having hitherto been unknown. The crystal was of a chocolate-brown colour, and like wiluite in type of form. There can be no doubt of its identity with xenotime.

*Fayalite*.—At the same locality, large uncrystallised masses occur of a mineral which may prove to be fayalite. The sp. gr. is 4.35, the colour brownish-black. It contains silica, iron, and traces of manganese and lime.

*Zircon*.—On a crystal of zircon from Burgess, Canada, the author has observed a new plane,  $\frac{1}{3}P$ .

*Rutile*.—Some very fine prisms of rutile of remarkable brilliancy have been recently found at Johnson's Mill, Alexander County, North Carolina. The planes  $P$ ,  $P\infty$ ,  $P3$ ,  $3P\frac{1}{2}$ ,  $\infty P$ ,  $\infty P3$ , and  $\infty P\infty$  were observed.

*Emeralds and Hiddenite*.—A new pocket of emeralds and hiddenite has been discovered on the Osborn Lackey land in Alexander Co.

B. H. B.

**New Minerals from Colorado.** By W. F. HILLEBRAND (*Amer. J. Sci.*, **29**, 340—341).—The author describes two new minerals, *zuniyite*

and *guitermanite*, from the Zuñi mine, Silverton, Colorado. Zunyite occurs in minute transparent tetrahedral crystals, having a hardness of 7 and sp. gr. of 2·875. The mean of a number of analyses of selected material is as follows:—

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	K <sub>2</sub> O.	Na <sub>2</sub> O.	Li <sub>2</sub> O.
24·33	0·20	57·88	0·10	0·24	trace
H <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	F.	Cl.	Less O for F and Cl.	Total.
10·89	0·60	5·61	2·91	3·02	99·74

The zunyite forms the gangue of an uncrystallised sulphide of lead and arsenic, to which the name *guitermanite* has been given. When fresh, it is of a bluish-grey colour, and possesses a slight metallic lustre; H. = 3; sp. gr. 5·94. An analysis gave the following results:—

S.	As.	Pb.	Cu.	Ag.	Fe.	Zunyite.	Total.
19·67	13·40	63·60	0·17	0·02	0·43	1·77	99·06

This leads to the provisional formula 3As<sub>2</sub>S<sub>3</sub>, 10PbS. B. H. B.

**Geological and Chemical Examination of the Kaolin Deposits of the South-western Provinces of Russia.** By A. M. WEINBERG (*Dingl. polyt. J.*, 255, 480—483).—Referring to the kaolin deposits situated in the south of Russia, it is stated that the rocks belong to the azoic formations, and consist of quartzites, gneiss, and felspathic granites. The depth of the deposits varies from 8—10 metres, whilst the beds comprise an area of 150 km. in length, and 80 km. in width. Two varieties of kaolin are found, one having a white, and the other a grey colour. On analysis the following percentages were obtained:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O and Na <sub>2</sub> O.	Loss by ignition.
Sudilkowo, white..	62·51	26·30	traces	0·72	0·13	0·79	9·49
„ grey ..	68·41	18·34	1·82	0·60	0·42	2·01	8·32
Dombrowka, white	67·65	23·53	traces	0·65	traces	0·32	7·70
„ grey.	68·71	18·60	1·84	0·83	0·14	4·07	6·32

*Soluble in Sulphuric Acid.*

	Sudilkowo, white.	Sudilkowo, grey.	Dombrowka, white.	Dombrowka, grey.
SiO <sub>2</sub> .....	18·00	15·97	23·80	15·90
Al <sub>2</sub> O <sub>3</sub> .....	25·59	15·74	21·70	15·10
Fe <sub>2</sub> O <sub>3</sub> .....	traces	1·82	traces	1·87

*Insoluble in Sulphuric Acid.*

SiO <sub>2</sub> .....	44·51	52·44	43·85	52·81
Al <sub>2</sub> O <sub>3</sub> .....	0·71	2·60	1·83	2·90
CaO and MgO....	0·85	1·02	0·65	0·97
Alkalis.....	0·79	2·01	0·32	4·07
Loss by ignition..	9·49	8·32	7·70	6·32

## Composition :

	Sudilkowo, white.	Sudilkowo, grey.	Dombrowka, white.	Dombrowka, grey.
Quartz .....	41.59	43.17	37.43	43.67
Felspar .....	5.25	14.90	9.22	17.08
Loss by ignition..	9.49	8.32	7.70	6.32
Clay substance (by difference) ....	43.67	33.61	45.65	32.93
				D. B.

**Meteoric Iron from Coahuila, Mexico.** By N. T. LUPTON (*Amer. J. Sci.*, 29, 232—233).—The analysis of a portion of a mass of iron, said to be a meteorite, found in the desert between Santa Rosa and the city of Chihuahua, gave the following results (I) :—

	Fe.	Ni.	Co.	P.	Cu.
I. ....	91.86	7.42	0.50	0.27	—
II. ....	92.95	6.62	0.48	0.02	trace

II is an analysis of a specimen of meteoric iron from Coahuila, given by Dr. Lawrence Smith in his "Scientific Researches." From the similarity of composition, in connection with other circumstances, it is evident that these are fragments of the same meteorite.

B. H. B.

## Organic Chemistry.

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**Preparation of Cyanogen Gas.** By G. JACQUEMIN (*Compt. rend.*, **100**, 1005—1006).—A concentrated solution of 1 part of pure potassium cyanide is allowed to drop, from a funnel provided with a stopcock, into a solution of 2 parts of cupric sulphate in 4 parts of water (see Gmelin's *Handbuch*). When the evolution of gas slackens the copper solution is heated in a water-bath. If commercial potassium cyanide is used, the gas contains small quantities of carbonic anhydride derived from the carbonate and cyanate present.

The insoluble cuprous cyanide formed in this reaction is washed by decantation, mixed with a solution of ferric chloride of about 30° A.B., and gently heated if necessary; or it is gently heated with manganese peroxide and acetic acid. In the first reaction ferrous chloride, cupric chloride, and cyanogen are formed, whilst in the second the products are manganous and cupric acetates and cyanogen.

C. H. B.

**Volatility of Cyano-derivatives containing Oxygen.** By L. HENRY (*Compt. rend.*, **100**, 1075—1077).—The substitution of O for H<sub>2</sub> in a CH<sub>3</sub> or CH<sub>2</sub> chain, or of N for H<sub>3</sub> in a CH<sub>3</sub> chain, produces a considerable rise in the boiling point of the compound, but the



change in volatility is very different when either of these substitutions, instead of taking place in an intact hydrocarbon chain, occurs in a chain in which the other of the two substitutions has already been effected. Compounds containing the terminal chain  $\text{CN}\cdot\text{CO}$ , have boiling points much lower than would be deduced from the analogy between their composition and that of corresponding compounds containing only the  $\text{CO}$  or the  $\text{CN}$  group. For example, propane,  $\text{CH}_3\text{Me}_2$ , boils at  $-17^\circ$ , and propionitril,  $\text{CH}_3\text{Me}\cdot\text{CN}$  at  $97-98^\circ$ , or a difference of  $+114^\circ$ , whereas acetone,  $\text{COMe}_2$ , boils at  $56^\circ$ , and acetic cyanide,  $\text{COMe}\cdot\text{CN}$ , at  $93^\circ$ , or a difference of only  $+37^\circ$ , and a similar difference is observed in the benzene series. The influence thus exerted on the boiling point by the contiguity of the oxygen and nitrogen is a remarkable example of *functional solidarity* in organic compounds. The contiguity of a  $\text{CO}$  group causes a considerable diminution in the rise of boiling point resulting from the substitution of  $\text{N}$  for  $\text{H}_3$  in a terminal  $\text{CH}_3$  chain. A precisely similar effect is observed in the substitution of cyanogen for chlorine. The increase in the boiling point is much greater when this substitution takes place in a haloïd ether group  $\text{CH}_2\text{Cl}$ , than when it occurs in an acid chloride group,  $\text{COCl}$ . For example the difference between the boiling points of ethyl chloride and ethyl cyanide is  $+85^\circ$ , whilst that between the boiling points of acetic chloride and acetic cyanide is only  $+41^\circ$ , and in the cases of benzyl chloride and benzyl cyanide, benzoic chloride and benzoic cyanide, the differences are  $+53^\circ$  and  $+10^\circ$  respectively. A comparison of the boiling points of these and similar compounds also shows that the displacement of  $\text{H}_2$  by  $\text{O}$  in a hydrocarbon chain already in direct union with a terminal cyanogen-group, produces a reduction, and not an increase in the boiling point of the compound.

It is important to note, however, that the influence thus exerted by the simultaneous presence of nitrogen and oxygen is only observed when the two elements are contiguous, or in other words are combined separately with two carbon-atoms which are in direct union. If the two carbon-atoms are separated by a  $\text{CH}_2$  group, the effect entirely disappears, hence it follows that the substitution of cyanogen for chlorine in a  $\text{CH}_2\text{Cl}$  group has the same effect on the boiling point, whether this group is in union with a hydrocarbon or an acid chain.

C. H. B.

**Synthesis of Tertiary Alcohols from Ketones.** By A. SAYTZEFF (*J. pr. Chem.* [2], **31**, 319—320).—The investigations of Beilstein and Rieth (*Annalen*, **126**, 246), of Butlerow (*Zeits. anal. Chem.*, 1864, 385), and of Pawlow (this Journal, 1877, ii, 732), have shown that certain ketones, all of which contain a methyl-group, when acted on by zinc organic compounds form condensation-products. The author has found that under similar treatment, ketones which do not contain a methyl-group yield zinc compounds, from which by subsequent treatment with water, tertiary alcohols can be obtained. Thus *ethyl dipropyl carbinol* has been obtained from dipropyl ketone, zinc, and ethyl iodide; and *triethyl carbinol* from diethyl ketone; and from dipropyl ketone, by the action of zinc and methyl iodide, *methyl dipropyl carbinol* has been prepared.

P. P. B.

**Preparation of Polyhydric Alcohols and their Derivatives by Means of Hypochlorous Acid.** By S. REFORMATSKY (*J. pr. Chem.* [2], 31, 318—319).—A hexyl glycerol, probably identical with that described by Orloff (*J. Russ. Chem. Soc.*, 1884 [1], 379), has been prepared by treating allyl dimethyl carbinol with hypochlorous acid, converting the chlorhydrin into the oxide, and treating this with water.

Diallyl carbinol treated in a similar manner yields the oxide of the pentahydric alcohol,  $C_7H_{11}(OH)_5$ . It is proposed to prepare other polyhydric alcohols in a similar manner. P. P. B.

**Inversion of Cane-sugar.** By W. OSTWALD (*J. pr. Chem.* [2], 31, 307—317).—The author has already pointed out (this vol., p. 3) the existence of a direct ratio between the electric conductivity of an acid and its affinity, as measured by the rate at which it inverts cane-sugar, and in a later communication (*ibid.*, 323) has shown the electric conductivity to be influenced by the state of dilution of the acid. In this paper, it is shown that the rate of inversion is influenced in a similar manner and almost to the same extent by the state of dilution of the acids. In the case of the weaker acids, the proportion between the constants of inversion and the electric conductivity is almost constant, but is increased slightly by the state of dilution; with the stronger acids the influence of dilution is more marked. A strict proportionality does not exist, and experiment has shown that one disturbing element in this problem is the amount of sugar present relatively to the amount of the acid. P. P. B.

**Primary Haloid Derivatives of Ethyl Ether.** By L. HENRY (*Compt. rend.*, 100, 1007—1009).—*Moniodo-ether*, obtained by the action of ethylene iodide on alcohol, reacts energetically with sodium ethoxide, forming ethoxy-ethylene,  $CH_2 : CH \cdot OEt$ , boiling at  $35^\circ$ , and ethylene diethoxide,  $C_2H_4(OEt)_2$ , boiling at  $121$ — $122^\circ$ . This reaction shows that moniodo-ether has the constitution  $CH_2I \cdot CH_2 \cdot OEt$ . No acetal is formed in the reaction, as Baumstark has stated.

Moniodo-ether, when purified by distillation over finely divided silver, remains unaltered under ordinary conditions, but if imperfectly purified it rapidly becomes brown. Its sp. gr. at  $0^\circ$  is 1.6924, and its vapour-density is 6.91 (calc. 6.91). It is insoluble in, and is unaltered by, water. Alcoholic potash attacks it energetically, yielding the same products as sodium ethylate. Metallic sodium produces the same decomposition on heating, but finely divided silver is without action even on boiling.

*Monobrom-ether*,  $CH_2Br \cdot CH_2 \cdot OEt$ , is obtained by the action of an excess of bromine on the preceding compound. It forms a colourless limpid liquid, with a sharp agreeable odour. It is very stable when exposed to light, and is neither dissolved nor decomposed by water. It boils at  $127$ — $128^\circ$ , under a pressure of 755 mm.; sp. gr. at  $0^\circ = 1.3704$ ; vapour-density, 5.29 (calc. 5.28). With alcoholic potash or sodium ethoxide, it behaves like the iodo-derivative. With potassium cyanide, it yields a nitrile and ethylene cyanide, and with antimony pentachloride it forms a solid compound, from which

the monobrom-ether can be completely recovered by treatment with water.

*Monochlor-ether*,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OEt}$ , is obtained from the iodo-derivative by the action of chlorine, antimony pentachloride, or iodine monochloride in presence of water. It is strictly analogous in its properties to the bromo-derivative, and boils at  $107\text{--}108^\circ$  under ordinary pressure; sp. gr. at  $0^\circ = 1.0572$ ; vapour-density, 3.73 (calc. 3.74). It is a very stable compound, and is not altered by exposure to light or contact with water.

The only corresponding ethylenic derivative hitherto known is the chloro-derivative,  $\text{CHMeCl}\cdot\text{OEt}$ , obtained by Wurtz and Frappoli. By means of a similar reaction, the author has prepared the corresponding bromo-derivative, which is a colourless unstable liquid, boiling at  $105^\circ$ ; sp. gr. at  $12^\circ = 1.0632$ . It dissolves in water, and is rapidly decomposed by it.

C. H. B.

**Products of Reduction of Dehydrotriacetonamine.** By F. CANZONERI and B. SPICA (*Gazzetta*, **15**, 1—4).—In this paper, the effect of various reducing agents on dehydrotriacetonamine is discussed; if tin and hydrochloric acid or hydriodic acid is used, the reduction is incomplete, but by sodium amalgam the dehydrotriacetonamine is converted into a substance whose chemical and physical properties agree with those of tetramethylpiperidine. It is, however, mixed with a small quantity of lower homologue, doubtless due to a partial decomposition, since all the higher derivatives of piperidine have a tendency to be resolved into simpler derivatives.

V. H. V.

**Preparation of Methyl Chloroformate.** By W. HENTSCHEL (*Ber.*, **18**, 1177).—This substance is most conveniently prepared by allowing methyl alcohol to flow, drop by drop, into liquid carbonyl chloride contained in a reflux apparatus immersed in a freezing mixture.

A. J. G.

**Oxidation of the Fatty Acids of Tallow by Potassium Permanganate in Alkaline Solution.** By M. GRÖGER (*Ber.*, **18**, 1268—1270).—When the fatty acids of tallow, after saponification with potash, are warmed with potassium permanganate, a mixture of insoluble oxy-fatty acids of the general formula  $\text{C}_n\text{H}_{2n}\text{O}_p$  is obtained; as yet only one acid, namely  $\text{C}_{26}\text{H}_{52}\text{O}_6$ , has been separated in a state of purity. This acid forms colourless crystals having a silky lustre, and melting at  $122.5^\circ$ ; when heated more strongly it volatilises with decomposition. It is insoluble in water, very sparingly soluble in ether, very readily soluble in hot and moderately in cold alcohol. The *silver salt*,  $\text{C}_{26}\text{H}_{51}\text{AgO}_6$ , forms a white flaky precipitate. It is probable that the acid is formed from oleic acid rather than from palmitic or stearic acids, as by using a large excess of potassium permanganate unchanged stearic acid was recovered, as well as acids conceivable as derivatives of palmitic acid.

N. H. M.

**Diazo-compounds of the Fatty Series: Diazoacetic Acid; Diazoacetamide; Pseudodiazoacetamide.** By T. CURTIUS (*Ber.*, **18**, 1283—1293).—The formation of diazoacetamide by the action of

ammonia on ethyl diazoacetate has been described (Abstr., 1884, 987). The ethereal salts of diazoacetic acid behave as feeble acids; they dissolve in aqueous alkalis, and can be recovered after remaining for a short time; on longer standing they break up into alcohol and salts of diazoacetic acid. These metallic salts are stable only when in solution; on evaporating their solutions, they give off nitrogen. Dilute acids and carbonic anhydride decompose the salts with evolution of nitrogen. When methyl diazoacetate,  $\text{CHN}_2\cdot\text{COOMe}$ , is shaken with 10 times the quantity of ammonia (25 per cent. solution) for five weeks, being all the time exposed to a winter temperature, yellow crystals of the *ammonium salt of pseudodiazoacetamide* separate; the filtrate from these crystals yields *diazoacetamide*,  $\text{CHN}_2\cdot\text{CONH}_2$ . The latter compound crystallises from water in yellow transparent crystals melting, with evolution of gas, at  $114^\circ$ . When heated suddenly, it detonates. It is decomposed by dilute soda, with evolution of ammonia and nitrogen. It precipitates mercury and silver from solutions of their salts. When acted on by iodine, it gives off nitrogen and yields diiodoacetamide,  $\text{CHI}_2\cdot\text{CONH}_2$ ; this when heated becomes yellow at  $170^\circ$ , partly sublimes at  $185\text{--}190^\circ$ , softens at  $198^\circ$ , and melts with evolution of iodine at  $201\text{--}202^\circ$ . It dissolves very sparingly in alcohol, but readily in tincture of iodine. Boiling hydrochloric acid does not act on it, and it is with difficulty decomposed by hot concentrated potash. Its formation from diazoacetamide

shows the latter compound to have the constitution  $\begin{array}{c} \text{N} \\ | \\ \text{N} \rangle \text{CH}\cdot\text{CONH}_2. \end{array}$

*Pseudodiazoacetamide*,  $(\text{C}_2\text{H}_3\text{N}_3\text{O})_3$ , is obtained from its ammonium salt dissolved in well cooled water, by precipitation with glacial acetic acid. It forms a yellow crystalline powder, sparingly soluble in cold water, dilute hydrochloric acid, and in glacial acetic acid, and is decomposed by long contact with these solvents, with evolution of nitrogen. Iodine acts on it with difficulty, and without formation of diiodoacetamide. It reduces silver salts only on heating. It melts at  $170^\circ$ ; if heated quickly it detonates. With Fehling's solution, it gives a green colour. When warmed with water, the yellow solution becomes colourless, and deposits a white crystalline substance which is sparingly soluble in water, but readily soluble in dilute soda. The *ammonium salt of pseudodiazoacetamide*,  $(\text{C}_2\text{H}_3\text{N}_3\text{O})_3\cdot 2\text{NH}_3$ , forms lemon-yellow needles, melting with decomposition at  $155^\circ$ ; it is decomposed by contact with water, in which it is sparingly soluble. The *silver salt*,  $(\text{C}_2\text{H}_3\text{N}_3\text{O})_3\text{Ag}_2 + 1\frac{1}{2}\text{H}_2\text{O}$ , is obtained as a voluminous yellow precipitate; on warming, it becomes black and is reduced. The *mercury salt* forms a very stable greenish-yellow powder, very sparingly soluble in cold water; the solution yields mercury on boiling. All three salts detonate when quickly heated. The *copper* and *lead salts* were prepared.

When pseudodiazoacetamide is boiled with dilute hydrochloric acid, nitrogen is evolved, and ammonium chloride is found in the solution. Four of the nitrogen-atoms in the compound are present as diazo-groups, whilst of the remaining five nitrogen-atoms, four had been converted into ammonia.

If the product from the preparation of diazoacetamide and pseudo-diazoacetamide is evaporated in a vacuum, the whole of the latter compound is converted into diazoacetamide. N. H. M.

**Symmetrical Dimethylsuccinic Acid (Hydropyrocinchonic Acid).** By C. A. BISCHOFF and C. RACH (*Ber.*, **18**, 1202—1203).—Beckurts and Otto have recently stated that hydropyrocinchonic acid is identical with symmetrical dimethylsuccinic acid (this vol., p. 754). The authors had independently arrived at the same conclusion, having synthesised the acid in the following ways: (1) by methylating ethyl propenyltricarboxylic acid, and heating the tribasic acid,  $\text{CMe}(\text{COOH})_2\cdot\text{CHMe}\cdot\text{COOH}$ , prepared from the product; (2) by decomposition of the compound  $\text{CMe}(\text{COOEt})_2\cdot\text{CMe}(\text{COOEt})_2$ , obtained by the methylation of ethyl acetylenetetracarboxylate, or by the action of iodine on ethylic methylsodomalonate, or by the action of ethylic methylsodomalonate on ethylic methylchlormalonate; (3) by the reduction of pyrocinchonic acid prepared from ethylic acetosuccinate and hydrocyanic acid. A. J. G.

**Derivatives of Diazosuccinic Acid.** By T. CURTIUS and F. KOCH (*Ber.*, **18**, 1293—1301).—Hydrochlorides of normal ethereal salts of aspartic acid are prepared by the action of hydrochloric acid on aspartic acid dissolved in boiling alcohol, whilst the acid ethereal salts are obtained by the action of hydrochloric acid on a cold alcoholic solution of aspartic acid. *Monethyl aspartate hydrochloride* forms large colourless needles melting at  $199^\circ$ . *Diethyl aspartate hydrochloride* crystallises from alcohol in groups of needles which soften at  $95^\circ$ ; it is very hygroscopic. *Dimethyl aspartate hydrochloride* forms lustrous prisms; it is also very hygroscopic.

When equal molecules of the diethyl salt and sodium nitrite are dissolved in ice-water and a few drops of dilute sulphuric acid are added, a turbidity is produced by the formation of *diethyl diazosuccinate*; this is extracted with ether and the operation repeated until sulphuric acid produces no more turbidity. The ethereal solution, after being washed with soda and with water, yields on evaporation a yellow oil containing 75 per cent. of diethyl diazosuccinate; the impurities are ethyl fumarate and *ethyl azinsuccinate*. *Diethyl diazosuccinate*,  $\text{COOEt}\cdot\text{CH}_2\text{CN}_2\cdot\text{COOEt}$ , resembles ethyl diazoacetate (*Abstr.*, 1884, 987), but is less stable. By spontaneous decomposition, it gives off part of its nitrogen, and yields *diethyl azinsuccinate*,  $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_8$ ; when boiled with water, it gives off all its nitrogen with formation of diethyl fumarate. From this reaction the authors consider the

constitution 
$$\begin{array}{c} \text{N} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{N} \end{array} \begin{array}{l} \text{COOEt} \\ \\ \text{CH}_2\cdot\text{COOEt} \end{array}$$
 as the most probable. By the action

of ammonia upon diethyl diazosuccinate, ethyl diazosuccinamate,  $\text{C}_6\text{H}_5\text{N}_3\text{O}_3$ , and fumaramide are formed.

*Fumaramide*,  $\text{CONH}_2\cdot\text{CH}:\text{CH}\cdot\text{CONH}_2$ , crystallises from boiling water in small white tufts of needles, melting at  $232^\circ$ . *Ethyl diazosuccinamate*,  $\text{NH}_2\text{CO}\cdot\text{CN}_2\cdot\text{CH}_2\cdot\text{COOEt}$ , crystallises from ether

in thin gold-coloured prisms, an inch long, and melts at 110—112° with evolution of gas. When heated quickly, it detonates. It dissolves sparingly in cold ether and ice-water, but readily in hot water and alcohol. It is not decomposed by boiling with pure water, but is at once decomposed by glacial acetic acid, and by dilute soda in the cold. It reduces silver and copper from solutions of their salts. *Methyl azinsuccinate*,  $C_{12}H_{16}N_2O_8$ , is formed when methyl diazosuccinate is allowed to stand for a few days; on mixing with ether the compound separates in white needles having a silky lustre, and melting at 149—150°. Methyl azinsuccinate is sparingly soluble in cold, readily in hot water and alcohol; it is sparingly soluble in boiling ether. The aqueous solution on long boiling is found to contain free azinsuccinic acid. It does not give off nitrogen or ammonia when boiled with acids or alkalis. When boiled with baryta, the *barium salt*,  $C_8H_4N_2O_8Ba_2$ , is formed. It is, therefore, the methyl salt of a tetrabasic acid, and probably has the constitution  $N_2[C(COOMe)CH_2COOMe]_2$ . *Azinsuccinic acid* is very readily soluble in alcohol and in water; it crystallises with difficulty. Its salts are almost all sparingly soluble; the barium salt forms a fine yellowish-white powder sparingly soluble in all solvents.

N. H. M.

#### Formation of Ethyl Azinsuccinate from Ethyl Diazoacetate.

By T. CURTIUS (*Ber.*, 18, 1302—1304).—Ethyl diazoacetate, when heated to 130°, gives off three-fourths of its nitrogen, thus:— $4CHN_2COOEt = C_8H_4N_2O_8Et_4 + 3N_2$ . The *ethyl salt* so obtained was converted into a barium salt,  $C_8H_4N_2O_8Ba_2$ , which resembles barium azinsuccinate obtained from diazosuccinic acid (see preceding Abstract) in appearance as well as in composition. On the other hand, the methyl salt of the acid obtained from diazosuccinic acid is crystalline (m. p. 149—150°), whilst that of the acid obtained from diazoacetic acid is a syrup. The acids are distinguished provisionally by the names  $\alpha$ - and  $\beta$ -azinsuccinic acid. The constitution

$$\begin{array}{c} \text{COOH}\cdot\text{CH} \quad \text{CH}\cdot\text{COOH} \\ | \quad \quad \quad | \\ \text{COOH}\cdot\text{CH} \quad \text{CH}\cdot\text{COOH} \end{array} \text{N} \text{---} \text{N} \begin{array}{c} \text{CH}\cdot\text{COOH} \\ | \\ \text{CH}\cdot\text{COOH} \end{array}$$

is suggested as the most probable one for  $\beta$ -azinsuccinic acid (obtained from diazoacetic acid).

N. H. M.

**Amides of the Oxalic Series.** By L. HENRY (*Compt. rend.*, 100, 943—946).—The author has prepared pyrotartaramide and adipamide by means of the ordinary general method of preparation. The first five amides of this series illustrate in a marked manner the difference between members containing an even number and those containing an odd number of carbon-atoms.

*Oxamide*: crystalline powder; infusible; soluble in 2700 parts of water at 7·3°.

*Malonamide*: easily crystallisable; melts at 168—170°; soluble in 12 parts of water at 8°.

*Succinamide*: crystalline powder; melts at 242—243°; soluble in 160 parts of water at 9·1°.

*Pyrotartaramide*: crystallises in large lamellæ; melts at 175°; soluble in 14 parts of water at 10·4°.

*Adipamide*: crystalline powder; melts at  $220^{\circ}$ ; soluble in 227 parts of water at  $12.2^{\circ}$ .

The even-carbon members of the series crystallise with difficulty, melt only at high temperatures, and are but slightly soluble in water; whilst the odd-carbon members crystallise readily, melt at much lower temperatures, and are comparatively easily soluble. In both groups the fusibility increases with the molecular weight, since the introduction of  $\text{CH}_2$  chains causes the amide to approximate more closely to a hydrocarbon in constitution, but the effect produced by each successive introduction of  $\text{CH}_2$  becomes less and less marked as the series is ascended.

*Symmetrical Dimethyl Amides*.—The author has prepared the dimethyl amides of malonic, pyrotartaric, and adipic acids by the action of an aqueous solution of methylamine on the ethyl salts at the ordinary temperature. The action of the methylamine is much more rapid than that of ammonia under the same conditions. All the dimethyl amides crystallise readily in plates, lamellæ, or needles, and are much more soluble in water than the corresponding simple amides. The odd-carbon members are, however, much more soluble than the even-carbon members, and are also much more easily fusible. The melting points of the dimethyl amides are as a rule much lower than those of the simple amides, and approach very closely to the melting points of the acids.

*Even-carbon Members.*

	M. p.
Dimethyloxamide .....	$209-210^{\circ}$
Dimethylsuccinamide .....	$175^{\circ}$
Dimethyladipamide .....	$151-153^{\circ}$

*Odd-carbon Members.*

	M. p.
Dimethylmalonamide .....	$123-125^{\circ}$
Dimethylpyrotartaramide .....	$113-115$

C. H. B.

**Thiotolen and Thiophen.** By V. MEYER (*Ber.*, **18**, 1326—1330). Theoretical.

**Isomeric Thiophensulphonic Acids.** By J. LANGER (*Ber.*, **18**, 1114—1116). (Continued from Abstr., 1884, 1133.)—When  $\beta$ -thiophensulphonic chloride is boiled with water it is decomposed into hydrogen chloride and  $\beta$ -thiophendisulphonic acid,  $\text{C}_4\text{SH}_2(\text{SO}_3\text{H})_2$ , which forms yellowish crystals easily soluble in water, and having an acid taste and reaction; the barium salt,  $\text{C}_4\text{SH}_2 \cdot (\text{SO}_3)_2 \cdot \text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$ , crystallises in pearly scales. An attempt was made to obtain  $\beta$ -thiophendisulphonic iodide by gradually dropping diiodothiophen into pyrosulphuric acid ( $\text{H}_2\text{S}_2\text{O}_7$ ); if the operation is performed slowly and carefully very little or no iodine vapour is evolved, and the reaction appears to take place easily; the result, however, seems to consist of a mixture of  $\beta$ -thiophendi- and mono-sulphonic iodides; neither compound was, however, isolated.

A. P.

**Phenyl Cyanate and Hydrogen Chloride.** W. HENTSCHEL (*Ber.*, 18, 1178).—The author denies the accuracy of Leuckart's statement that by the action of carbonyl chloride on aniline hydrochloride, a compound of the formula  $\text{COCl}_2 \cdot 2\text{NPh} : \text{CO}$  is formed, and confirms his own earlier statement (*Abstr.*, 1884, 1002) that hydrochloride of phenyl cyanate,  $\text{NPh} : \text{CO}, \text{HCl}$ , is formed. This substance is also obtained as a crystalline mass, melting at  $45^\circ$ , by the action of hydrogen chloride on phenyl cyanate.

A. J. G.

**Influence of Light on the Course of Chemical Reactions in the Bromination of Aromatic Compounds.** By J. SCHRAMM (*Ber.*, 18, 1272—1279).—In a former communication (this vol., p. 518), the author mentioned that bromine, in small quantities, has no action on ethylbenzene in the dark; he now finds that when an excess of bromine is used, a reaction does take place, with formation of a mixture of ortho- and para-ethylbromobenzene. An analogous reaction takes place with propylbenzene in the dark. When bromine (1 mol.) acts on propylbenzene in direct sunlight, *phenylbromopropane*, probably  $\text{CHBrEtPh}$ , is formed; this, by the further action of bromine in sunlight, yields a dibromide, *ethylphenyldibromomethane*,  $\text{CBr}_2\text{EtPh}$ . Bromine also acts in the dark on the monobromide, yielding allylbenzene bromide,  $\text{CHBrPh} \cdot \text{CHBrMe}$ . Butylbenzene is acted on by bromine in an analogous way. By the action of bromine on paraxylene in the dark, monobromoparaxylene and a small quantity of dibromoparaxylene [ $\text{Me} : \text{Me} : \text{Br} : \text{Br} = 1 : 4 : 3 : 6$ ] are formed. When bromine (1 mol.) is added to paraxylene in diffused daylight, monobromoparaxylene, together with small quantities of xylyl bromide and xylylene bromide are formed. In direct sunlight, bromine acts very violently on paraxylene; 1 mol. bromine reacts with formation of paraxylyl bromide and a trace of paraxylylene bromide; whilst by the action of 2 mols. bromine paraxylylene bromide is produced. Meta- and ortho-xylene react in an analogous manner with bromine.

N. H. M.

**Ortho-ethyltoluene.** By A. CLAUS and F. MANN (*Ber.*, 18, 1121—1124).—Ortho-ethyltoluene is formed by treating equal parts of orthobromotoluene, ethyl bromide, and ether with metallic sodium. It is a colourless oil, boiling at  $158$ — $159^\circ$  (uncorr.), sp. gr. =  $0.8731$  at  $16^\circ \text{C}$ ., and may be cooled to  $-17^\circ$  without solidifying; when oxidised with dilute nitric acid, it yields nitrotoluic acid; this is white, and melts at  $103^\circ$  (uncorr.). Ortho-ethyltoluene is readily oxidised by chromic acid, carbonic anhydride being given off; but the oxidation is not complete as is usually the case with benzene-derivatives in which the ortho-position is occupied by one of the radicles of the fatty series. By oxidation with an alkaline solution of potassium permanganate, no phthalic acid is formed, but although ethyltoluene is quite free from any para-compounds, a minute quantity of terephthalic acid can always be detected; this occurs whether the oxidation is rapid or slow; the authors consider it to be due to a secondary action similar to that by which benzoic and terephthalic acids are formed in the forced oxidation of benzene.

A. P.



**Derivatives of the three Isomeric Xylenes.** By RADZISZEWSKI and P. WISPEK (*Ber.*, 18, 1279—1282).—The authors have repeated their experiments on the xylenes, having found that the method of preparation previously employed (*Abstr.*, 1882, 1283) did not yield pure products. The results now given are partly new and partly corrections of those given previously. *Paraxylyl bromide* melts at 35.5°. *Paraxylylene bromide* melts at 143.5°. *Paraxylyl cyanide*, prepared from the bromide by the action of potassium cyanide, is a colourless liquid having a strong aromatic odour; on cooling it solidifies and melts again at 18°; it boils at 242—243°; sp. gr. 0.9922 at 22°. *Paratoluyllacetamide* is obtained from paraxylyl cyanide by the action of hydrogen peroxide and potash with the aid of slight heat; it forms white lustrous plates melting at 184°; dissolves sparingly in cold water and in ether, readily in boiling alcohol and water, and sublimes without decomposition. *Paratoluyllacetic acid* melts at 91°.

*Orthoxylyl bromide* crystallises from well-cooled ether in lustrous quadratic plates melting at 21°. *Orthoxylylene bromide* was found to have the melting point 94.5°, ascribed to it by Baeyer and Perkin. *Orthoxylyl cyanide* is a colourless liquid, boiling at 244°; sp. gr. 1.0156 at 22°. *Orthotoluyllacetamide* melts at 161°; it sublimes unchanged; it dissolves sparingly in ether and in cold water, readily in boiling alcohol and water. *Orthotoluyllacetic acid* melts at 88—89°. *Metaxylyl bromide* boils at 212—215°. *Metaxylylene bromide* has the melting point 77° ascribed to it by Colson. *Metaxylyl cyanide* is a colourless liquid, boiling at 240—241°; sp. gr. 1.0022 at 22°. *Metaxylyllacetamide* forms flat needles which dissolve sparingly in ether and cold water, more readily in boiling alcohol and water. It melts at 141°, and sublimes unchanged. *Metatoluyllacetic acid* melts at 61°.

N. H. M.

**Trichlorophenol: Trichloronitro- and Trichloramido-phenols: Tribromonitro- and Tribromamido-phenols.** By G. D'ACCOMO (*Ber.*, 18, 1163—1164; 1164—1166; 1166—1167; and 1167—1169).—Trichlorophenol has the constitution  $[\text{OH} : \text{Cl} : \text{Cl} : \text{Cl} = 1 : 2 : 4 : 6]$ , as by treatment with ferric chloride it yields unsymmetrical tetrachlorobenzene, and can be prepared by the action of chlorine on ortho- and para-dichlorophenol respectively. The following derivatives were prepared:—*Propionyltrichlorophenol*,  $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{OCOEt}$ , a colourless strongly refracting liquid, boiling at 262.5—264.5° (uncorr.). *Butyryltrichlorophenol*,  $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{OCOPr}$ , a liquid which resembles the above, and boils at 272—275° (uncorr.). *Valeryltrichlorophenol*,  $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{OCOC}_4\text{H}_9$ , also a colourless strongly refracting liquid; it boils at 281—284° (uncorr.) *Benzoyltrichlorophenol*,  $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{OBz}$ , crystallising in light colourless needles, which melt at 70°; it is insoluble in water, soluble in alcohol, and very readily soluble in ether, alcohol, and light petroleum. *Phthalyltrichlorophenol*,  $\text{C}_6\text{H}_4(\text{COO}\cdot\text{C}_6\text{H}_2\text{Cl}_3)_2$ , a crystalline powder, insoluble in water, sparingly soluble in alcohol and ether, readily soluble in light petroleum and chloroform; it melts at 193—194°.

*Trichloronitrophenol*,  $\text{NO}_2\cdot\text{C}_6\text{HCl}_3\cdot\text{OH}$ , is obtained by the action of potash upon ortho- or meta-nitrobenzoyltrichloronitrophenol. It

crystallises in needles, dissolves readily in alcohol, ether, chloroform, and benzene, but sparingly in water, and gives a violet-blue colour with ferric chloride. The *ammonium salt*, obtained by dissolving trichloronitrophenol in dilute ammonia, forms gold-coloured needles. The *silver salt* forms small yellow needles.

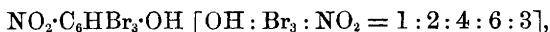
By acting on benzoyltrichlorophenol with a mixture of nitric and sulphuric acids, two dinitro-derivatives, *trichloronitrophenyl meta- and ortho-nitrobenzoate*, are formed. The *meta-compound* is the chief product; it forms large colourless plates melting at  $146.3^{\circ}$  (corr.), dissolves in alcohol, ether, chloroform, and benzene; is insoluble in water, and decomposes at  $290^{\circ}$ . The *ortho-compound* forms lustrous colourless spangles, soluble in alcohol, ether, &c., melts at  $106.1^{\circ}$  (corr.), and decomposes completely at  $245^{\circ}$ .

By acting on benzoyltrichlorophenol with nitric acid alone, *trichlorophenyl metanitrobenzoate*,  $C_6H_2Cl_3O \cdot CO \cdot C_6H_4 \cdot NO_2$ , is obtained. It crystallises from ether in large monoclinic prisms, melting at  $131-132^{\circ}$ , and is soluble in alcohol, chloroform, and benzene. When saponified, it yields trichlorophenol and metanitrobenzoic acid. A substance melting at  $164-165^{\circ}$  is found in the mother-liquor from the preparation of this compound.

The potassium, magnesium, and barium salts of trichlorometanitrophenol were prepared.

*Trichlorometamidophenol*,  $NH_2 \cdot C_6HCl_3 \cdot OH$ , forms splendid silky light colourless needles, melting at  $95^{\circ}$ ; dissolves sparingly in cold, but readily in hot water; by long boiling with water it is decomposed. It is also readily soluble in alcohol, ether, chloroform, and benzene. With ferric chloride, it gives a violet-red, and with calcium hypochlorite a dirty red coloration. Its properties are more acid than basic; it does not yield a stable hydrochloride or sulphate. By the action of ethyl nitrite, a diazo-compound is formed, which yields the original trichlorophenol; the constitution of trichloramidophenol is therefore  $[OH : Cl_3 : NH_2 = 1 : 2 : 4 : 6 : 3]$ .

*Tribromometanitrophenol*,



was prepared by saponifying ortho- or meta-nitrobenzoyltribromometanitrophenol with potash; it forms a heavy colourless crystalline powder, very sparingly soluble in hot water, readily in alcohol, ether, benzene, and chloroform, and melts at  $89^{\circ}$ . Its aqueous solution scarcely gives the phenol reaction with ferric chloride, and does not give Liebermann's reaction. It decomposes carbonates. The *ammonium, barium, magnesium, and potassium salts* are described.

*Benzoyltribromophenol*,  $C_6H_2Br_3 \cdot OCOPh$ , crystallises in small colourless prisms melting at  $81.5^{\circ}$ ; it is almost insoluble in water, soluble in alcohol, readily soluble in ether, chloroform, and light petroleum. *Metanitrobenzoyltribromonitrophenol* forms very minute colourless lustrous needles melting at  $153.8^{\circ}$  (corr.). *Orthonitrobenzoyltribromonitrophenol* also crystallises in very small colourless needles; it melts at  $129.2^{\circ}$  (corr.), and decomposes at  $215^{\circ}$ . By the action of potash it yields tribromonitrophenol and orthonitrobenzoic acid.

*Tribromometamidophenol*,  $NH_2 \cdot C_6HBr_3 \cdot OH$ , forms splendid silky

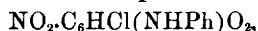
needles, which soon turn brown on exposure to light; it dissolves sparingly in cold water, readily in alcohol, ether, &c., and melts at  $115^{\circ}$ . The aqueous solution gives with ferric chloride a green, with calcium hypochlorite a dirty red colour. By treatment with ethyl nitrite and subsequently boiling the product with alcohol, the original tribromophenol was obtained.

The tribromometanitrophenol here described is probably identical with that obtained by Lindner (this vol., p. 775), although Lindner's tribromometanitrophenol melts at  $85^{\circ}$ , and yields a barium salt with only 1 mol.  $\text{H}_2\text{O}$ . N. H. M.

**Chloronitro- and Bromonitro-quinones.** By J. GUARESCHI and G. DACCOMO (*Ber.*, 18, 1170—1177).—By acting on propionyltrichlorophenol with nitric and sulphuric acids, *dichloronitroquinone*,



and *propionyltrichloronitrophenol* are formed. *Dichloronitroquinone* forms microscopic yellow needles, sparingly soluble in water, soluble in warm alcohol, readily soluble in chloroform. It reduces potassium permanganate when boiled with it, reacts with hydroxylamine, giving a red colour, and gives an intense blood-red colour with paratoluidine and with aniline. *Monochloronitroquinone anilide*,



obtained by the action of aniline on dichloronitroquinone, forms rhombic plates melting at  $206$ — $208^{\circ}$ . The constitution of the compound would be  $[\text{Cl} : \text{NO}_2 : \text{PhNH} = 2 : 3 : 6 \text{ or } = 6 : 2 : 3]$ .

*Propionyltrichloronitrophenol*,  $\text{NO}_2 \cdot \text{C}_6\text{HCl}_3\text{OC}_3\text{H}_5\text{O}$ , crystallises from alcohol in splendid colourless needles melting at  $65^{\circ}$ . When treated with potash, it yields trichloronitrophenol, identical with that obtained from benzoyltrichloronitrophenol (this vol., p. 889). By the action of the nitrating mixture on propionyltrichloronitrophenol, or on acetyl-, butyryl-, and valeryl-trichlorophenol, a further quantity of dichloronitroquinone was formed.

*Propionyltribromophenol*,  $\text{C}_6\text{H}_2\text{Br}_3\text{O} \cdot \text{C}_3\text{H}_5\text{O}$ , was obtained by the action of propionic chloride on tribromophenol; it forms long white needles melting at  $65^{\circ}$ , almost insoluble in cold water, sparingly soluble in benzene, and readily soluble in ether and chloroform. When treated with the nitrating mixture, it yielded *dibromonitroquinone* and *propionyltribromonitrophenol*. *Dibromonitroquinone* forms yellow rectangular plates, melting with decomposition at  $244$ — $246^{\circ}$ , sparingly soluble in hot water and in cold alcohol. With aniline and with paratoluidine, it gives an intense blood-red colour; with hydroxylamine an orange-red colour. *Propionyltribromonitrophenol* forms colourless lustrous scales, melting at  $70$ — $71^{\circ}$ , almost insoluble in water, sparingly soluble in benzene, soluble in alcohol, and readily soluble in ether and in chloroform.

When propionylphenol is added to the nitrating mixture, a violent reaction takes place with formation of metadinitrophenol; no nitroquinone was formed.

The formation of dichloro- and dibromo-nitroquinone from trichloro- and tribromo-nitropropionylphenol respectively, proves that by the

direct nitration of a halogen-derivative of phenol a product can be formed in which the nitro-group takes up the position 3 or 5, these being the only possible positions for the nitro-group to have taken up in the case just mentioned. This fact had not previously been shown, and such a substitution had been considered impossible.

N. H. M.

**Formation of Quinones from Paramethylamines.** By E. NÖLTING and T. BAUMAN (*Ber.*, **18**, 1150—1152).—Amidoparamethylated amines yield quinones of the next lower homologue when treated with an excess of a mixture of chromic and sulphuric acids. The yield is, however, not large except in the case of amidomesitylene, which is readily converted into isoxyloquinone, the yield being about 40 per cent. Quinones were prepared from paratoluidine, amido-isoxylene, amido-orthoxylylene, amidopseudocumene, and isoduridine. The quinone from the last-mentioned base is obtained as an oil which, when treated with sulphurous acid, is converted into the quinol  $C_6HMe_3(OH)_2$ ; this substance is sparingly soluble in cold water, crystallises in magnificent white needles, melts at  $169^\circ$ , and is readily soluble in the usual solvents; on oxidation, the quinone is again obtained as a yellow oil, which when cooled crystallises in radial masses and melts at  $11^\circ$ .

A. P.

**Paranitro-orthocresol and Toluquinonechlorimide.** By R. HIRSCH (*Ber.*, **18**, 1511—1515).—According to Hofmann and v. Miller (*Abstr.*, 1881, 592) the nitration of orthocresol yields a mixture of dinitrocresol (m. p.  $86^\circ$ ) and orthonitrocresol (m. p.  $69.5^\circ$ ), with paranitro-orthocresol, an oil boiling at  $226\text{--}230^\circ$  and distilling with steam, from which amidocresyl methyl ether (m. p.  $52\text{--}53^\circ$ ) could be prepared. The author has entirely failed to obtain a substance having these properties, and finds on the contrary that *paranitro-orthocresol* is formed in the reaction, but is a solid that does not distil with steam. It is dimorphous, crystallising in groups of needles melting at  $82\text{--}85^\circ$ , or in hexagonal plates melting at  $79\text{--}80^\circ$ ; it resolidifies at  $74\text{--}75^\circ$ . It is readily soluble in alcohol, acetic acid, and benzene, sparingly soluble in water and light petroleum. The yield is about 12 per cent. of the cresol employed. When further nitrated, both orthonitro- and paranitro-orthocresol yield the same dinitrocresol [ $OH : NO_2 : NO_2 : Me = 1 : 2 : 4 : 6$ ].

*Paramidorthocresol* is prepared by reducing the nitro-compound with tin and hydrochloric acid. It crystallises in silvery plates, melts at  $175^\circ$ , and can be distilled; is readily soluble in acids and alkalis, and yields toluquinone when oxidised.

*Toluquinonechlorimide*,  $C_6H_4ClNO$ , is obtained by oxidising an aqueous solution of amidocresol hydrochloride with bleaching powder. It crystallises in needles, melts at  $87\text{--}88^\circ$ , and explodes at  $100\text{--}115^\circ$ ; it distils with steam, but at the same time is partially decomposed. It is much more stable than quinonechlorimide, its lower homologue; long boiling with water converts it into a chlorinated toluquinol (?) crystallising in silvery plates; by boiling for many hours with hydrogen sodium sulphite, it is converted into amidocresolsulphonic acid. With phenol or naphthol and sulphuric acid, it yields substances which must

be regarded as the homologues of the dyes obtained in Liebermann's reaction. The investigation of the products formed by the action of aqueous soda on the substance is still incomplete. An intermediate oxidation-product of amidocresol, of a cherry-red colour, was obtained, but not further investigated. A. J. G.

**Derivatives of Pseudocumidine.** By E. NÖLTING and T. BAUMAN (*Ber.*, 18, 1145—1150).—By replacing amidogen by bromine in pseudocumidine, a monobromopseudocumene,  $C_6H_2Me_3Br$ , is obtained identical with that prepared directly from pseudocumene.

When heated with glacial acetic acid, pseudocumidine yields *acetocumidine*,  $C_6H_2Me_3\cdot NH\cdot Ac$ ; it crystallises in white needles, is readily soluble in alcohol, sparingly in water, and melts at  $161^\circ$ .

*Diazoamidopseudocumene*,  $C_6H_2Me_3\cdot N_2\cdot NH\cdot C_6H_2Me_3$ , is obtained by treating a mixture of pseudocumidine and diazocumene with sodium acetate in glacial acetic acid solution; it forms clear yellow tablets, melts at  $130\cdot5^\circ$ , and is soluble in the usual solvents.

The *amidoazopseudocumene*,  $C_6H_2Me_3\cdot N_2\cdot C_6HMe_3\cdot NH_2$ , is obtained as the hydrochloride by warming diazoamidopseudocumene with pseudocumidine and its hydrochloride for about four hours at  $60$ — $80^\circ$ ; the free base crystallises in orange scales, melts at  $138$ — $139^\circ$ , and is readily soluble in the usual solvents; it is decomposed by water into hydrochloric acid and the free base; the same decomposition takes place slowly on exposure to air; it is soluble in phenol with a yellowish-brown colour, whilst the amidoazo-compound in which the diazo-group is in the para-position to the amido-group gives a red or violet, and the ortho-compound a green coloration. When reduced with stannous chloride, pseudocumidine and cumeyldiamine,  $C_6HMe_3(NH_2)_2$  [ $Me_3 : (NH_2)_2 = 1 : 2 : 4 : 5 : 6$ ], are formed; the latter crystallises in white needles, is unaltered by the air, and melts at  $90$ — $92^\circ$ ; it is but little soluble in cold water, but readily in hot, as it is also in alcohol, ether, &c.; its hydrochloric acid solution gives a red colour with ferric chloride, and on distillation a yellow quinone-like substance is carried over, soluble in soda with a violet colour. On heating the hydrochloride with benzaldehyde, hydrogen chloride is evolved.

*Amidotetramethylbenzene*,  $C_6HMe_4\cdot NH_2$ ,

[ $NH_2 : Me : Me : Me : Me = 1 : 2 : 4 : 5 : 6$ ],

is obtained by heating pseudocumidine hydrochloride with methyl alcohol for 10 hours at  $200^\circ$ , and then for 10—12 hours at  $300^\circ$ ; it boils at  $250^\circ$  under 740 mm. pressure. The *hydrochloride* forms small white prisms readily soluble in water. The *acetyl compound*,  $C_6HMe_4\cdot NH\cdot Ac$ , forms white needles, melts at  $210$ — $211^\circ$ , is sparingly soluble in water, readily in alcohol. It is identical with the compound obtained by Hofmann from the high boiling bye-products in the preparation of crystallised cumidine (*Abstr.*, 1884, 1320). Mesitylene hydrochloride on similar treatment yields the same compound.

A. P.

**Azo-derivatives of Thymol.** By G. MAZZARA and G. POSSETTÖ (*Gazzetta*, 15, 52—55).—By treating aniline dissolved in hydrochloric

acid with potassium nitrite and an alkaline solution of thymol, a dark red precipitate is produced consisting of monophenylazothymol,  $\text{PhN}_2\cdot\text{C}_6\text{H}_2\text{MePr}\cdot\text{OH}$ , and phenyldiazothymol,  $(\text{PhN}_2)_2\text{C}_6\text{HMePr}\cdot\text{OH}$ , of which the former is soluble in potash, the latter insoluble. The former crystallises in brilliant reddish-yellow prismatic needles melting at  $85\text{--}90^\circ$ , whilst the latter is deposited from a chloroform solution in the form of minute silky needles melting at  $168^\circ$ . V. H. V.

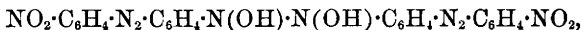
**Intermediate Reduction-products of the Nitroazo-compounds.** By J. W. JANOVSKY and L. ERB (*Ber.*, **18**, 1133—1138).—The mono- and di-nitrazobenzene obtained by Laurent (*Ann. Chem. Pharm.*, **75**, 73) by the nitration of azobenzene are both para-compounds. Mononitrazobenzene,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  [ $\text{N}_2 : \text{NO}_2 = 1 : 4$ ], melts at  $140^\circ$ , and yields paraphenylenediamine and aniline when reduced with tin and hydrochloric acid. *Diparadinitrazobenzene*,



melts at  $206^\circ$ ; it may be crystallised from glacial acetic acid. On reduction, it yields paraphenylenediamine. The red oil obtained at the same time by Laurent is metadinitrazobenzene,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  [ $\text{NO}_2 : \text{N}_2 : \text{NO}_2 = 3 : 1 : 3$ ], it is soluble in the usual solvents, and after standing for some time solidifies at  $15^\circ$  to an orange-red mass; by reduction with tin and hydrochloric acid it yields metaphenylenediamine melting at  $63^\circ$ , and with potassium nitrite it yields a phenylene-brown. *Trinitrazobenzene* may be obtained by nitrating either mono- or di-paranitrazobenzene or azobenzene with fuming nitric acid; it may be crystallised from acetone or alcohol, and is obtained in long sulphur-yellow needles; it melts at  $169^\circ$  to a red fluid, which explodes when heated above its melting point. By heating paradinitrazobenzene with fuming nitric acid, a second trinitrazobenzene is obtained which crystallises in yellow silky needles; it is less soluble in alcohol than its isomeride, and melts at  $180^\circ$ ; on complete reduction both these compounds yield paraphenylenediamine.

If ammonium sulphide and a fixed alkali are added to the hot alcoholic solution of any of the above-mentioned nitrazo-compounds, a beautiful blue coloration is obtained, which is only destroyed on prolonged heating. By the action of aqueous ammonium sulphide or other reducing agents on the hot solutions of the nitrazo-compounds, azobenzenenitrolic acids are formed.

The *paranitrolic acid*,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{OH})\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{Ph}$ , obtained from paramononitrazobenzene, crystallises from alcohol in small reddish-brown needles; it dissolves in the aqueous solutions of the alkalis with an intense blue colour, its salts are very unstable, the free acid being precipitated from the alkaline solution by carbonic anhydride; by oxidation with an alkaline solution of potassium ferricyanide, nitrazobenzene is again formed. The *nitronitrolic acid*,  $\text{C}_{12}\text{H}_9\text{N}_4\text{O}_3 =$

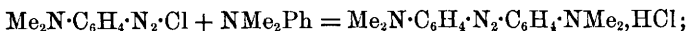


obtained from dinitrazobenzene, crystallises from acetone in brilliant monoclinic amber-coloured crystals having a bluish fluorescence; it melts at  $218^\circ$ , and is very readily soluble in aqueous solutions of the

alkalis, being reoxidised to diparadinitrazobenzene. With nitric acid a nitro-compound is obtained, forming fine crystals similar to those of metanitrilaniline; by further heating with ammonium sulphide, a nitrolic compound is obtained which crystallises in brown needles and yields a blue colour with alkalis. By the partial reduction of metadinitrazobenzene, an oily nitrolic acid was obtained, which also yields the colour reaction with alkalis. A. P.

**Crystalline Bases from Methyl-violet.** By H. WICKELHAUS (*Ber.*, 18, 1270—1272).—The bases of methyl-violet obtained from different sources are shown, by measurements of their crystals, not to be identical; this is contrary to the opinion expressed by Hofmann (this vol., p. 791). N. H. M.

**Azylines.** By E. NÖLTING (*Ber.*, 18, 1143—1145).—On treating diazoparadimethylaniline hydrochloride with dimethylaniline, the hydrochloride of tetramethylazyline is obtained—



the base is obtained on recrystallisation in red needles: it melts at 262—265°, and corresponds completely with the tetramethylazyline prepared by Lippman and Fleisner (*Ber.*, 16, 1415 and 2768); this method of preparation, therefore, confirms their views as to the constitution of these compounds. A. P.

**Structure of Hydroxylamine-derivatives.** By W. LOSSEN (*Ber.*, 18, 1189—1202).

**Amidoximes and Azoximes.** By F. TIEMANN (*Ber.*, 18, 1060—1062).—A review of the results gained in the investigation of these two classes of compounds. A. J. G.

**Action of Sodium Amalgam on Aqueous Solutions of Benzenylamidoxime.** By F. TIEMANN and E. NAGELI (*Ber.*, 18, 1086—1087).—It has been already shown that benzaldehyde and ammonia are formed in this reaction (*Abstr.*, 1884, 1325). It is probable that benzaldoxime is formed as an intermediate product. The reaction is very incomplete, the benzaldehyde formed only amounting to 10—12 per cent. of the amidoxime employed, the greater part of which remains unaltered. A. J. G.

**Derivatives of Benzenylamidoxime.** By P. KRÜGER (*Ber.*, 18, 1053—1060). (Compare *Abstr.*, 1884, 734, 1325, this vol., p. 790).—Benzenylamidoxime crystallises in long, flat prisms or in plates which melt at 79—80°. It has a neutral reaction, dissolves in both acids and alkalis, and is not decomposed by them even on boiling. Heated with hydrochloric acid at 200°, it is decomposed into benzoic acid and ammonium chloride. By careful heating, it can be distilled, but if heated quickly it is decomposed at 170° into benzonitrile and ammonia. Nitrous acid converts it into benzamide. It gives a red coloration with ferric chloride, and is a powerful poison. The *hydrochloride*

crystallises in concentrically grouped flat prisms; the *hydrogen sulphate*,  $C_7H_5N_2O.H_2SO_4$ , forms large prisms; the normal sulphate,  $(C_7H_5N_2O)_2.H_2SO_4$ , is an amorphous mass. The *sodium salt*,  $NH_2.CPh:NO.Na$ , forms a hygroscopic white mass; there are two *potassium salts*,  $NH_2.CPh:NO.K$  and  $NH_2.CPh:NOH$ . The salts of the alkaline earths form crystalline powders. The *copper salt*,  $NH_2.CPh:NO.Cu.OH$ , is obtained as an amorphous bluish-green precipitate; the silver salt is a very unstable crystalline powder. The ethereal salts are obtained by the action of the respective iodides on the sodium salt; they are stable, yield salts with acids, and when heated with hydrochloric acid at above  $100^\circ$  yield benzoic acid, ammonia, and hydroxylamine ethers. The *methyl salt*,  $NH_2.CPh:NOMe$ , crystallises in prisms and melts at  $230^\circ$ ; the *ethyl salt* crystallises in plates and melts at  $67^\circ$ ; the *benzyl salt* crystallises in long scales and melts at  $90.5^\circ$ . These salts are converted into the oxime chlorides when treated with hydrochloric acid and sodium nitrite.

*Benzenylmethoxime chloride*,  $CPhCl:NOMe$ , is an oil of agreeable odour, it does not solidify at  $-10^\circ$ , and boils at  $225^\circ$  (uncorr.). *Benzenylethoxime chloride*,  $CPhCl:NOEt$ , boils at  $230^\circ$  (uncorr.). *Benzenylbenzoxime chloride*,  $CPhCl:NOCH_2Ph$ , is a heavy oil; it cannot be distilled alone, but distils with steam.

*Ethyl benzhydroximate*,  $HO.CPh:NOEt$ , is obtained as a yellow oil by the action of sodium nitrite on an aqueous solution of the ethyl salt of benzenylamidoxime. It is soon decomposed by water into benzoic acid and ethylhydroxylamine.

*Benzenylphenyluramidoxime*,  $NHPh.CO.NH.CPh:NOH$ , is prepared by the action of carbanil on benzenylamidoxime; it crystallises in white plates and melts at  $115^\circ$ . It does not unite with acids or bases.

*Benzenylphenylthiouramidoxime*,  $NHPh.CS.NH.CPh:NOH$ , is prepared by the action of phenylthiocarbamide on benzenylamidoxime; it crystallises in pale yellow plates and melts at  $163^\circ$ . A. J. G.

**Metanitrobenzenylamidoxime.** By M. SCHÖPF (*Ber.*, **18**, 1063—1067).—*Metanitrobenzonitrile* is prepared by nitrating benzonitrile at a temperature not exceeding  $25^\circ$ . It crystallises in silky needles, and melts at  $117^\circ$ .

*Metanitrobenzenylamidoxime*,  $NO_2.C_6H_4.C(NH_2):NOH$ , is obtained by heating a mixture of hydroxylamine hydrochloride, metanitrobenzonitrile, and aqueous soda for five hours at  $100^\circ$ . It crystallises in orange needles, melts at  $174^\circ$ , is readily soluble in hot water and alcohol, moderately soluble in ether, benzene, and chloroform, and is insoluble in light petroleum. It shows the reactions characteristic of amidoximes. The hydrochloride,  $C_7H_7N_3O_3.HCl$ , forms a white, crystalline mass. The platinochloride,  $(C_7H_7N_3O_3)_2.H_2PtCl_6$ , crystallises in orange prisms. The ethyl salt,  $NO_2.C_6H_4.C(NH_2):NOEt$ , prepared by the action of ethyl iodide on the sodium salt, crystallises in yellow prisms, melts at about  $70^\circ$  (?), and cannot be distilled. The benzyl salt forms yellow plates and melts at  $58^\circ$ .

The ethylcarbamate-derivative,  $NO_2.C_6H_4.CN_2H_5O.CO.OEt$ , prepared by the action of ethyl chlorocarbonate on the amidoxime, crystallises in white needles and melts at  $152-153^\circ$ .



*Metanitrobenzenylazoximethenyl*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{---} \text{N} \end{smallmatrix} \text{CMe}$ , is prepared by dissolving nitrobenzenylamidoxime in acetic anhydride, and separates on cooling in white needles. It melts at  $109^\circ$ , can be sublimed without decomposition or distilled with steam, is moderately soluble in water, readily in alcohol and ether, and is not attacked by acids or alkalis.

*Metanitrobenzenylazoximebenzenyl*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{---} \text{N} \end{smallmatrix} \text{CPh}$ , is obtained by the action of benzoic chloride on nitrobenzenylamidoxime. It crystallises in white needles, melts at  $160^\circ$ , is insoluble in water and light petroleum, soluble in alcohol, ether, and benzene, and is not affected by acids or alkalis.

A. J. G.

**Action of Acetic, Propionic, and Butyric Acids, Chlorides, and Anhydrides on Benzenylamidoxime.** By O. SCHULZ (*Ber.*, **18**, 1080—1086).—When benzenylamidoxime is heated with acetic, propionic, or butyric acid, it yields dibenzenylazoxime and benzamide.

*Acetylbenzenylamidoxime*,  $\text{NH}_2 \cdot \text{CPh} : \text{NO} \cdot \text{Ac}$ , is formed by the action of acetic chloride on an ethereal solution of benzenylamidoxime. It crystallises in thin plates or flat prisms, melts at  $96^\circ$ , and is very unstable, readily suffering decomposition into benzenylazoximethenyl. *Propionylbenzenylamidoxime*,  $\text{NH}_2 \cdot \text{CPh} : \text{NO} \cdot \text{COEt}$ , melts at  $93^\circ$ . *Butyrylbenzenylamidoxime*,  $\text{NH}_2 \cdot \text{CPh} : \text{NO} \cdot \text{COPr}^a$ , crystallises in slender needles, and melts at  $94^\circ$ .

*Benzenylazoximpropenyl*,  $\text{CPh} \begin{smallmatrix} \text{N} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{---} \text{N} \end{smallmatrix} \text{CEt}$ , is prepared by heating benzenylamidoxime with propionic anhydride; it is a nearly colourless liquid of aromatic odour, and boils at  $255^\circ$ . *Benzenylazoximbutenyl*,  $\text{CPh} \begin{smallmatrix} \text{N} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{---} \text{N} \end{smallmatrix} \text{CPr}^a$ , prepared in a similar manner from normal butyric anhydride, boils at  $265^\circ$ .

A. J. G.

**Phenylethenylamidoxime.** By P. KNUDSEN (*Ber.*, **18**, 1068—1074).—Starting from benzyl cyanide, this compound and its derivatives were prepared by methods described by Tiemann, Krüger, and others (*Abstr.*, 1884, 734, 1325, and preceding Abstracts).

*Phenylethenylamidoxime*,  $\text{CH}_2\text{Ph} \cdot \text{C}(\text{NH}_2) : \text{NOH}$ , crystallises in thin prisms, melts at  $67^\circ$ , is destitute of odour, and yields salts with acids and bases. The *hydrochloride*,  $\text{C}_8\text{H}_{10}\text{N}_2\text{O} \cdot \text{HCl}$ , crystallises in flat prisms, and melts at  $155^\circ$ . The *benzoyl*-derivative,



crystallises in prisms, and melts at  $144^\circ$ ; the acetyl-derivative melts at  $124^\circ$ . The *ethyl* salt,  $\text{CH}_2\text{Ph} \cdot \text{C}(\text{NH}_2) : \text{NOEt}$ , crystallises in flat prisms, and melts at  $58^\circ$ . The *benzyl* salt crystallises in compact prisms, and melts at  $55^\circ$ .

*Phenylethenylazoximebenzenyl*,  $\text{CH}_2\text{Ph} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{---} \text{N} \end{smallmatrix} \text{CPh}$ , crystallises in needles, melts at  $82^\circ$ , is insoluble in water, and is not affected by acids or bases.

*Phenylethenylazoximethenyl*,  $\text{CH}_2\text{Ph}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}\text{CMe}$ , forms a yellowish-brown oil, boiling at  $262^\circ$ .

*Phenylethenylphenyluramidoxime*,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NH}\cdot\text{CO}\cdot\text{NHPh})\text{:NOH}$ , crystallises in silvery plates, melts at  $123^\circ$ , and is soluble in benzene, alcohol, ether, and light petroleum. A. J. G.

**Phenylhydroxyethenylamidoxime.** By F. GROSS (*Ber.*, 18, 1074—1080).—This substance and some of its derivatives have been described by Tiemann (*Abstr.*, 1884, 734). It melts at  $158\text{--}159^\circ$ , not at  $140^\circ$ , as previously stated. The sodium salt crystallises in needles. The ethyl salt,  $\text{HO}\cdot\text{CHPh}\cdot\text{C}(\text{NH}_2)\text{:NOEt}$ , crystallises in concentrically grouped needles, and melts at  $89^\circ$ ; the benzyl salt crystallises in small white needles, and melts at  $102\text{--}103^\circ$ .

*Phenylhydroxyethenylazoximethenyl*,  $\text{HO}\cdot\text{CHPh}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}\text{CMe}$ , is prepared by heating the acetyl-derivative on the water-bath; it crystallises in needles, is sparingly soluble in cold water, readily in alcohol, ether, and benzene, and can be distilled.

*Diacetylphenylazoximethenylamidoxime*,  $\text{AcO}\cdot\text{CHPh}\cdot\text{C}(\text{NH}_2)\text{:NOAc}$ , obtained by heating phenylhydroxyethenylamidoxime with acetic chloride, crystallises in small, short prisms, and melts at  $113^\circ$ .

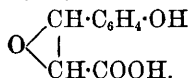
*Acetoxyphenylethenylazoximethenyl*,  $\text{AcO}\cdot\text{CHPh}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}\text{CMe}$ , is obtained by heating phenylhydroxyethenylamidoxime with a large excess of acetic chloride or anhydride. It crystallises in slender white needles, melts at  $52^\circ$ , and distils unaltered. It is nearly insoluble in cold water, very readily soluble in alcohol, ether, and benzene.

*Benzoylphenylhydroxyethenylamidoxime*,  $\text{HO}\cdot\text{CHPh}\cdot\text{C}(\text{NH}_2)\text{:NOBz}$ , is prepared by the action of benzoic chloride on the amidoxime; it forms slender white needles, and melts at  $148\text{--}149^\circ$ . When heated with acetic chloride, it yields the corresponding acetoxy-compound,  $\text{AcO}\cdot\text{CHPh}\cdot\text{C}(\text{NH}_2)\text{:NOBz}$ , which forms small crystals, and melts at  $165^\circ$ . A. J. G.

**Condensation of Salicylaldehyde with Hippuric Acid.** By J. PLÖCHL and L. WOLFRUM (*Ber.*, 18, 1183—1188).—When salicylaldehyde and hippuric acid are allowed to remain for some weeks with an excess of acetic anhydride, a condensation product,  $\text{C}_{32}\text{H}_{24}\text{O}_7\text{N}_2$ , is formed, analogous to that already obtained by Plöchl (*Abstr.*, 1884, 604) from benzaldehyde and hippuric acid. The compound melts at  $160^\circ$ . By repeated crystallisation from solvents containing water, such as ordinary alcohol, it successively takes up and eliminates the elements of water, yielding at last *benzoylimidocoumarin*. The same change is more conveniently effected by boiling for an hour with glacial acetic acid containing a few drops of strong hydrochloric acid.

*Benzoylimidocoumarin*,  $\text{O}\begin{smallmatrix} \text{C}_6\text{H}_4\cdot\text{CH} \\ | \\ \text{CO}\cdot\text{CH} \end{smallmatrix}\text{NBz}$ , melts without decomposition at  $170\text{--}171^\circ$ . It is insoluble in water, but dissolves in warm ether, alcohol, benzene, and glacial acetic acid. It is attacked by

dilute acids and alkalis only when heated, and then but slowly; by treatment with strong soda solution until no more ammonia is given off, it is converted into *salicylglycidic acid*,



This acid is sparingly soluble in cold, but readily in hot water, from which it crystallises in flat needles or prisms; it is also readily soluble in alcohol and ether. It is not stable, and after a time gives on the one hand salicylaldehyde, and on the other its anhydride, *oxycoumarin*. With ferric chloride, it gives an intense green colour, a reaction shared by almost all glycidic compounds. *Calcium salicylglycidate* crystallises in prisms with  $6\text{H}_2\text{O}$ , which become anhydrous at  $100^\circ$ .

Oxycoumarin,  $\text{O} \begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{CH} \\ | \\ \text{CO} \cdot \text{CH} \end{array} \text{O}$ , is formed by heating salicylglycidic

acid with dilute mineral acids. It melts without decomposition at  $152\text{--}153^\circ$ , is readily soluble in ether and in warm alcohol, and crystallises from the latter in lustrous prisms. On boiling with water, it is reconverted into salicylglycidic acid, which on long standing again parts with water. By the action of dry ammonia, an amide is formed, crystallising in prisms. By the reduction of salicylglycidic *salicyllactic acid*,  $\text{C}_9\text{H}_{10}\text{O}_4$ , is obtained; it is an almost colourless syrup, soluble in water in all proportions. It closely resembles salicylglycollic acid. The *zinc salt* and *calcium salt* (with  $6\text{H}_2\text{O}$ ) were prepared.

N. H. M.

### Nitro- and Sulpho-derivatives of Phenylamidoacetic Acid.

By J. PLÖCHL and W. LOË (*Ber.*, **18**, 1179—1182).—Erlenmeyer and Lipp have shown that in the nitration and sulphonation of phenylalanine, the entering groups occupy the para-position exclusively (*Abstr.*, 1883, 963), and Radziszewski (*Ber.*, **3**, 648), and later, Baeyer (*Abstr.*, 1878, 587), have shown that phenylacetic acid yields the ortho- and para-nitro-acids on nitration; it was therefore to be expected that phenylamidoacetic acid, the next lower homologue of phenylalanine, would also yield para-derivatives, but it is found that both the nitro and sulphonic groups assume the meta-position only.

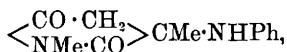
*Metanitrophenylamidoacetic acid*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH}$ , prepared by the action of nitric acid on a solution of phenylamidoacetic acid in sulphuric acid, crystallises in silky needles, melts at  $172^\circ$  with decomposition, and is very soluble in water. The copper salt,  $(\text{C}_8\text{H}_7\text{N}_2\text{O}_4)_2\text{Cu}$ , forms pale blue needles. To determine its constitution, it was converted by the diazo-reaction into the corresponding *nitromandelic acid*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$ , which on oxidation was completely converted into metanitrobenzoic acid and metanitrobenzaldehyde.

*Metamidophenylamidoacetic acid*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH}$ , is prepared by reducing the nitro-acid; it forms silvery plates, melts at  $214^\circ$  with decomposition, and yields salts with acids and bases.

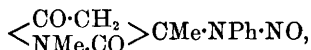
*Metasulphophenylamidoacetic acid*,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NH}_2)\cdot\text{COOH}$ , is formed by heating phenylamidoacetic acid with fuming sulphuric acid at  $120^\circ$ ; it crystallises in minute slender needles, is sparingly soluble in cold water, insoluble in alcohol and ether. When fused with potash, it yields metahydroxybenzoic acid. A. J. G.

**Anilidopyrotartaric Acid ( $\alpha$ -Methyl- $\alpha$ -anilidosuccinic Acid).** By M. SCHILLER-WECHSLER (*Ber.*, **18**, 1037—1052).—*Ethyl anilidopyrotartaramate*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CMe}(\text{NHPh})\cdot\text{CH}_2\cdot\text{COOEt}$ . When ethyl  $\beta$ -cyano- $\beta$ -hydroxybutyrate is treated with aniline, the corresponding anilido-compound is obtained as a reddish-yellow oil; this is slowly added to cold concentrated sulphuric acid, and the mixture, after some hours, is poured into cold water and neutralised, when *ethyl anilidopyrotartaramate* separates. It crystallises in lustrous white plates, melts at  $125^\circ$ , is readily soluble in water, alcohol, benzene, and chloroform, and insoluble in light petroleum.

*Anilidopyrotartarimide*,  $\langle \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{NH}\cdot\text{CO} \end{smallmatrix} \rangle \text{CMe}\cdot\text{NHPh}$ , is formed when ethyl anilidopyrotartaramate is heated for some time with water, alcohol, ammonia, alkalis, or acids. It crystallises in lustrous white prisms, melts at  $150^\circ$ , is soluble in alcohol, benzene, and chloroform, sparingly soluble in ether and cold water, insoluble in light petroleum, and yields salts with both acids and bases. The *acetyl*-derivative,  $\text{C}_{11}\text{H}_{11}\text{AcN}_2\text{O}_2$ , crystallises in white needles, and melts at  $235^\circ$ . The *benzoyl*-derivative,  $\text{C}_{11}\text{H}_{11}\text{BzN}_2\text{O}_2$ , forms white needles, and melts at  $190^\circ$ . The *nitroso*-derivative,  $\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}_2\cdot\text{NO}$ , crystallises in slender yellow needles, and melts at  $173^\circ$ . A *methyl*-derivative,



is obtained by the action of potash and methyl iodide on the imide; it crystallises in prisms, melts at  $103^\circ$ , is readily soluble in alcohol, ether, and benzene, and yields a *nitroso*-derivative,



crystallising in thick white needles, melting at  $147^\circ$ . By the continued action of methyl iodide and potash on the methyl-derivative, a permethylated anilidopyrotartaramide is obtained; the chloride forms a deliquescent crystalline mass, and the platinochloride has the formula  $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_2\text{Cl}_2\cdot\text{PtCl}_4$ .

*Anilidopyrotartaric acid*,  $\text{COOH}\cdot\text{CMe}(\text{NHPh})\cdot\text{CH}_2\cdot\text{COOH}$ , is obtained as hydrochloride by heating anilidopyrotartarimide (1 part) with a solution of potash (5 parts) in water, as long as ammonia is evolved, neutralising with hydrochloric acid, and evaporating on the water-bath. The free acid, prepared by decomposing the copper salt with hydrogen sulphide, crystallises with 1 mol.  $\text{H}_2\text{O}$  in white needles, melts at  $101$ – $102^\circ$ , is insoluble in benzene, light petroleum, and acetone, nearly insoluble in ether, readily soluble in hot water and alcohol. It gives precipitates with most salts of the heavy metals, and, when heated, reduces Fehling's solution and silver nitrate. The

hydrochloride,  $C_{11}H_{13}NO_4 \cdot HCl + H_2O$ , forms a white crystalline mass. The copper salt,  $C_{11}H_{13}NO_4 \cdot Cu + H_2O$ , is obtained as a bluish-green crystalline precipitate on adding copper sulphate and sodium acetate to the hydrochloride. The cuprammonium salt,  $C_{11}H_{13}NO_4 \cdot Cu \cdot NH_3$ , is obtained in clear green crystals on adding copper sulphate and ammonia to the hydrochloride; an argentammonium salt was also obtained.

*Toluidopyrotartarimide*,  $\langle \begin{smallmatrix} NH \cdot CO \\ CO \cdot CH_2 \end{smallmatrix} \rangle CMe \cdot NH \cdot C_6H_4Me$ , prepared in a manner similar to the anilido-compound, crystallises in white needles, melts at  $181^\circ$ , and resembles the anilido-compound in its reactions and properties.

When anilidopyrotartaric acid is submitted to dry distillation, it yields a condensation product,  $C_{11}H_5NO_2$ ; this crystallises in long silky needles, and melts at  $98^\circ$ , and when heated with alkalis is converted into a crystalline substance of strongly acid properties, melting at  $162$ – $163^\circ$ .

A. J. G.

**Crystallography of Phenylcoumarin and of Coumarin.** By E. SCACCHI (*Gazzetta*, 14, 563–570).—Phenylcoumarin forms long rhombic prisms, terminated by four faces, the suppression of one or more of which leads to several variations. These crystals appear from the symmetry of their faces to be monoclinic, with axial ratio  $a : b : c = 3.1054 : 1 : 3.0060$ , although the measurements do not indicate whether the crystals belong to the monoclinic or orthorhombic system; although the formation of twin crystals seems to preclude this latter view, yet this may be due to hemihedrism.

Coumarin crystallises in the orthorhombic system, with axial ratio  $a : b : c = 0.9833 : 1 : 0.3696$ .

V. H. V.

**Production of Hydroxycoumarin.** By D. BIZZARRI (*Gazzetta*, 15, 33–37).—As in the preparation of umbelliferone by v. Pechmann and Welsh's synthetical method (*Abstr.*, 1884, 1346) not more than 50 per cent. of the theoretical yield is obtained, the author has improved the process for the extraction of the crude product of the reaction; the method proposed is given in detail. If catechol and malic acid are heated with concentrated sulphuric acid, a violent reaction occurs, and a substance may be extracted from the product of the reaction crystallising in rose-coloured needles. It melts at  $280$ – $285^\circ$  with partial decomposition, and the analytical results agree with the formula of a metahydroxycoumarin,  $CH \langle \begin{smallmatrix} C_6H_3O(OH) \\ CH - CO \end{smallmatrix} \rangle O$ , probably isomeric with the metahydroxycoumarin obtained by v. Pechmann from quinol; the substituted groupings in the former are probably in the positions  $[CH : CHCO \cdot O : O : OH = 1 : 2 : 3]$ , but in the latter in the positions  $1 : 2 : 5$ . The metahydroxycoumarin is sparingly soluble in cold, easily soluble in hot water, alcohol, and acetic acid. It reduces salts of gold, copper, and silver, and forms various red coloured solutions with potash, and sulphuric and nitric acids.

V. H. V.

**$\beta$ -Sulphophthalic Acid.** By C. GRAEBE (*Ber.*, **18**, 1126—1130).— $\beta$ -Sulphophthalic acid,  $C_6H_4(SO_3H)(COOH)_2$ , appears to be identical with the acid of which Remsen describes the potassium salt (*Abstr.*, 1884, 319); it is prepared by oxidising an aqueous solution of dinitronaphtholsulphonic acid with nitric acid (sp. gr. = 1.30) at 100°. It is a clear yellow syrup, very difficult to crystallise, but which has been obtained in crystals containing 1 mol.  $H_2O$ ; it is readily soluble in water and alcohol, but is insoluble in ether. The barium salt,  $(C_6H_4SO_3)_2Ba_3 + 2H_2O$ , is pale yellow and difficult to crystallise. Fluoresceinsulphonic acid,  $C_{20}H_{11}O_6 \cdot HSO_3$ , is moderately soluble in hot water, readily in alcohol, insoluble in ether, it crystallises in reddish-yellow needles or prisms; its aqueous solution is of a yellow colour, and shows but slight fluorescence, whilst its alkaline solution has an intense green fluorescence; it acts as a tribasic acid. The calcium salt,  $(C_{20}H_9SO_3)_2Ca_3$ , is of a vermilion-red colour, and is easily soluble in water. Hydroxyphthalic acid,  $OH \cdot C_6H_3(COOH)_2$ , was prepared from sulphophthalic acid; it melts at 180—183°, and is converted into the anhydride, which melts at 164°; it yields a brownish-red coloration when treated with ferric chloride. A. P.

**Action of Phthalic Anhydride on Benzyl Cyanide.** By S. GABRIEL (*Ber.*, **18**, 1264—1265).—9 parts benzyl cyanide, 13 parts phthalic anhydride, and 2.5 parts of dry sodium acetate were boiled for two hours, allowed to cool, and then boiled with three times the volume of alcohol. On cooling, crystals of cyanbenzylidenephthalide,  $CO < \begin{smallmatrix} C_6H_4 \\ -O- \end{smallmatrix} > C : CPh \cdot CN$ , separate. This substance forms fine yellow needles melting at 164—165.5°, dissolves in soda only when boiled, giving off an odour of benzyl cyanide. It may be heated for 10 minutes with strong sulphuric acid at 100°, and with glacial acetic acid saturated with hydrochloric acid, at 170° for three hours without decomposition. When heated with alcoholic ammonia at 100°, ammonium phthalaminate and an oil smelling of benzyl cyanide are formed.

The mother-liquor obtained in the preparation of cyanbenzylidenephthalide contains phthalamide, formed by the action of ammonia (produced from benzyl cyanide by the action of the water liberated in the reaction) upon phthalic anhydride. N. H. M.

**Benzylidenephthalide.** By S. GABRIEL (*Ber.*, **18**, 1251—1263).—By the action of nitrous acid on benzylidenephthalide, a compound,  $C_{15}H_{10}N_2O_6$ , is formed, provisionally named dinitrobenzylidenephthalide,  $CO < \begin{smallmatrix} C_6H_4 \\ -O- \end{smallmatrix} > C(NO_2) \cdot CHPh \cdot NO_2$ . It is very unstable; it forms rhombic crystals melting at 110—113°. It dissolves in dilute soda, and is at the same time decomposed, yielding sodium nitrite and a sodium salt,  $CO < \begin{smallmatrix} C_6H_4 \\ -O- \end{smallmatrix} > C(ONa) \cdot CPhNa \cdot NO_2 + 2\frac{1}{2}H_2O$ , which readily loses  $1\frac{1}{2}$  mol.  $H_2O$ ; the last molecule of water cannot be expelled without decomposing the salt. In presence of dilute acids the salt decomposes into nitromethylbenzene,  $CH_2Ph \cdot NO_2$ , a liquid

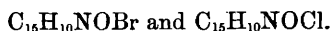
boiling at 225—227°, and *phthalic anhydride*. The formation of the latter puts beyond doubt the lactonic character of the compound. The salt may be boiled with excess of soda without decomposition.

Dinitrobenzylidenephthalide, when heated, is decomposed into nitrous acid and *nitrobenzylidenephthalide*; this, on further heating, at 210°, decomposes into phthalic anhydride and phenyl cyanate.

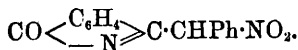
Nitrobenzylidenephthalide,  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} > \text{C} : \text{CPh} \cdot \text{NO}_2$ , forms yellowish plates, sparingly soluble in alcohol. It softens at 180°, melts at 195°, at the same time giving off gas, and when treated with soda yields the same salt as is obtained from dinitrobenzylidenephthalide.

By acting on benzylidenephthalide with ammonia, *phthalimidylbenzyl*,  $\text{C}_{15}\text{H}_{11}\text{NO}$ , is formed. This compound has been prepared by Gabriel and Michael (Abstr., 1879, 246) by the action of ammonia on desoxybenzoïncarboxylic acid. Ethylamine condenses with benzylidenephthalide *without* separation of water; the compound produced in this reaction is an *ethylamide* of *desoxybenzoïncarboxylic acid*. It forms colourless crystals, readily soluble in benzene, and melting at 139—140°. It reacts with hydroxylamine, forming an internal anhydride of *benzylphenylacetoximorthocarboxylic acid*,  $\text{C}_{15}\text{H}_{11}\text{NO}_2$ , which crystallises from its alcoholic solution in flat reddish needles, melting at 116—117°. This same compound is also obtained by the action of hydroxylamine upon desoxybenzoïncarboxylic acid.

*Phthalimidylbenzyl*,  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{N} \end{smallmatrix} > \text{C} \cdot \text{CH}_2\text{Ph}$ , when treated with bromine or phosphoric chloride, yields the substitution-products



The former crystallises in lustrous needles melting at 210—211°; the latter forms long slightly brown needles melting at 230—232°. By the action of nitrous acid on *phthalimidylbenzyl*, a compound,  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_4$ , and *phthalimidylnitrobenzyl*,  $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_3$ , crystallising in large yellow scales, melting at about 199°, are formed. When phthalimidylnitrobenzyl is heated, it gives off an odour of phenyl cyanate, does not give the nitroso-reaction with phenol and sulphuric acid, and dissolves in warm alkali. It probably has the constitution—



By reduction with hydriodic acid and amorphous phosphorus, phthalimidylbenzyl yields *benzylphthalidine*,  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NH} \end{smallmatrix} > \text{CH} \cdot \text{CH}_2\text{Ph}$ . It forms colourless scales, melting at 135—137°. When acted on by nitrous acid, *benzylnitrosophthalidine* is obtained; this compound forms yellow crystals, which melt at 92—93°, dissolve readily in benzene, light petroleum, and chloroform, and give the nitroso-reaction with phenol and sulphuric acid.

N. H. M.

**Cumenesulphonic Acid.** By A. CLAUS and L. TONN (*Ber.*, 18, 1239—1243).—100 parts of water at 16° dissolve about 4·5 parts of barium cumeneparasulphonate and about 16·5 parts of barium cumene-

$\beta$ -sulphonate. The para- is converted into the  $\beta$ -acid, not only when heated at  $100^\circ$ , but also on long contact with cold sulphuric acid.

*Cumene- $\beta$ -sulphonic acid* crystallises in small needles; the potassium, sodium, barium, lead, magnesium, zinc, and copper salts, are described. When the salts are heated with phosphoric chloride the sulphochloride is obtained as a viscid yellow oil, which, when treated in ethereal solution with ammonia yields cumene- $\beta$ -sulphonamide,  $C_9H_{11}\cdot SO_2NH_2$ , crystallising in needles and melting at  $127^\circ$ .

Oxidation experiments to determine the constitution of the  $\beta$ -acid did not lead to any very conclusive result, although metasulphobenzoic acid seems to be one of the products.

A. J. G.

**Preparation of Diamidotriphenylmethane.** By G. MAZZARA (*Gazzetta*, 15, 50—53).—The best method for the preparation of diamidotriphenylmethane is the one proposed by Fischer, which consists in heating aniline hydrochloride and benzaldehyde in presence of zinc chloride. But in this process some portion of the benzaldehyde combines with the diamidotriphenylmethane to produce the compound  $CHPh(C_6H_4N\cdot CHPh)_2$ . To render the change more complete the author proposes to substitute fuming hydrochloric acid for zinc chloride. Experiments are quoted to show that under these conditions nothing is formed, besides diamidotriphenylmethane, except a small quantity of a resinous matter which may be separated by adding a considerable proportion of water to the crude product of the reaction. Soda is then added to the filtrate to precipitate the diamidotriphenylmethane.

V. H. V.

**Azo-derivatives.** By G. MAZZARA (*Gazzetta*, 15, 44—50).—If a solution of diamidotriphenylmethane hydrochloride is treated with a solution of potassium nitrite, a yellowish amorphous precipitate is produced, insoluble in hydrochloric acid, ether, and benzene. Owing to its resinous nature, it could not be satisfactorily purified, but an analysis of its aurochloride pointed to the formula,  $CHPh(C_6H_4\cdot N_2ClAuCl_3)_2$ . If the solution of the above-mentioned diazo-derivative obtained by the action of potassium nitrite on diamidotriphenylmethane hydrochloride is added to a solution of potassium thymolate, a yellowish-red precipitate is produced; this, on purification, forms an amorphous black powder, melting at  $170^\circ$ . This substance is *dihydroxydimethyldiphenyldiazobenzophenylmethane*,  $CHPh[C_6H_4N_2\cdot C_6H_2MePr(OH)N]_2$ . When heated with phosphorous pentachloride it yields a dichlorinated derivative by the replacement of the two OH-groups by chlorine. In order to determine the constitution of the hydroxyl-derivative, it was heated with stannous chloride, and the product oxidised with ferric chloride, when thymoquinone was obtained, thus showing that the azo- and hydroxyl-groupings are in the 1 : 4 position.

V. H. V.

**Mononitro- $\beta$ -Naphthoic Acids.** By A. G. EKSTRAND (*Ber.*, 18, 1204—1209).—The author has repeated with larger quantities of material the experiments previously made by him (*Ber.*, 12, 1393) on these acids. By acting on  $\beta$ -naphthoic acid dissolved in glacial acetic



acid with fuming nitric acid, a product was obtained from which the three nitro-acids to be described were separated.

*Mononitro-β-naphthoic acid*, melting at 269°, forms fine colourless needles very readily soluble in alcohol. The *ethyl* salt forms small yellow plates which melt at 93° (uncorr.). By reduction of the acid with ferrous sulphate in ammoniacal solution, *amido-β-naphthoic acid* is obtained. It forms colourless needles, which melt at 211° (uncorr.). It dissolves readily in alcohol and becomes violet on exposure to air.

*Mononitro-β-naphthoic acid*, melting at 288—289°, crystallises in well-formed needles; it is sparingly soluble in alcohol. The *sodium* salt crystallises with 2 mols.  $H_2O$  in small greenish-yellow needles, very soluble in cold water. The *ethyl* salt forms long rhombic plates, rather sparingly soluble in alcohol and light petroleum; it melts at 122° (uncorr.) The corresponding *amido-β-naphthoic acid* forms colourless needles melting at 219° (uncorr.). The *hydrochloride*, *sulphate*, and *nitrate* of the amido-acid are described.

*Mononitro-β-naphthoic acid*, melting at 293°. This acid is identical with one previously obtained by the author (*loc. cit.*), to which he ascribed the melting point 280°, and with one obtained by Graeff (*Ber.*, 16, 2252) melting at 295°. The author assumes this latter to be the *corrected* melting point. The *sodium* salt (with 2 mols.  $H_2O$ ) and *calcium* salt (with 3 mols.  $H_2O$ ) are described. The *ethyl* salt forms long slender yellow needles melting at 110—111° (uncorr.). The *amido-β-naphthoic acid*, obtained by reduction of the nitro-acid, forms small lustrous scales, rather readily soluble in alcohol, melting at 232° (uncorr.); it soon becomes violet coloured. The *hydrochloride* of the amido-acid, which forms long violet needles, the *nitrate*, and the *sulphate* were prepared. *Calcium amido-β-naphthoate* forms short lilac-coloured prisms; it crystallises from water, in which it is readily soluble, with 4 mols.  $H_2O$ . The author has not yet isolated the mononitro-β-naphthoic acid melting at 220°, which he previously obtained (*loc. cit.*); he intends continuing the investigation.

N. H. M.

**Retene.** By E. BAMBERGER and S. C. HOOKER (*Ber.*, 18, 1024—1030, and 1030—1036).—A continuation of Bamberger's researches (*Abstr.*, 1884, 1040, and this vol., p. 549). The substance previously described as retistenequinone,  $C_{16}H_{14}O_2$ , has been found to be in reality *retenequinone*,  $C_{18}H_{16}O_2$ , the error being caused by the impossibility of completely burning this substance with copper oxide. The formulæ of all the derivatives of retenequinone previously described (*loc. cit.*) will require a corresponding alteration. The formula now assigned to the substance explains the reactions obtained with it by Ekstrand (*Abstr.*, 1884, 1041). The bromide,  $C_{10}H_8Br_4O_6$ , described by Ekstrand, is a mixture of dibromretenequinone and retenequinone. The pure dibromo-derivative,  $C_{18}H_{14}BrO_2$ , can be obtained by employing excess of bromine and vigorous agitation.

When reteneketone is distilled with zinc-dust, there is obtained, not retene as stated by Ekstrand, but retenefluorene,  $C_{17}H_{18}$ . This substance closely resembles retene in all its physical properties, but is distinguished from it by its behaviour with chromic and acetic acids,

by which it is completely oxidised, whilst retene yields retenequinone.

Oxidation products can only be obtained from freshly precipitated amorphous retenequinone.

*Oxyisopropyldiphenyleneketonecarboxylic acid*,  $C_{17}H_{14}O_4$ , is prepared by oxidising retenequinone with an alkaline solution of potassium permanganate. It crystallises in lustrous golden-yellow needles, melts at  $190^\circ$ , is sparingly soluble in ether, moderately in alcohol, readily in acetic acid, and is a strong monobasic acid. The *silver* salt,  $C_{17}H_{13}O_4Ag$ , forms voluminous yellow flocks. The *barium* salt,  $(C_{17}H_{13}O_4)_2Ba + 2H_2O$ , crystallises in yellow needles. When the ammonium salt is treated with hydroxylamine hydrochloride, the corresponding *ketoxime* acid is obtained as a yellowish-white precipitate. The silver, lead, barium, copper, and mercury salts are described.

*Diphenyleneketonedicarboxylic acid*,  $C_{15}H_{10}O_5$ , is obtained together with the acid above described by the oxidation of retenequinone. By heating the product with chromic mixture, the oxyisopropyl acid is completely converted into diphenylketonedicarboxylic acid. It crystallises in lustrous golden-yellow needles, does not melt at  $270^\circ$ , and is sparingly soluble in alcohol and ether, more readily in acetic acid. The *ethyl* salt,  $C_{19}H_{16}O_5$ , forms golden-yellow needles, and melts at  $114.5^\circ$ ; the *methyl* salt melts at  $184^\circ$ . *Diphenyleneketoximedicarboxylic acid*,  $C_{15}H_9NO_5$ , prepared by the action of hydroxylamine hydrochloride on the ammonium salt, forms straw-yellow flocks. Several of its salts are described.

*Diphenyleneketonecarboxylic acid*,  $C_{14}H_8O_3$ , is obtained by distilling the dicarboxylic acid or its silver salt, diphenylene ketone being also formed in the latter case. It crystallises in pale yellow needles, and gives a voluminous yellow silver salt,  $C_{14}H_7O_3Ag$ , a pale yellow barium salt, and a bright yellow ketoxime acid.

*Diphenyltricarboxylic acid*,  $C_{15}H_{10}O_6$ , is prepared by fusing diphenyleneketonedicarboxylic acid with potash. It forms a crystalline powder, is not altered by heating at  $270^\circ$ , is nearly insoluble in water, readily soluble in alcohol and ether. The *silver* salt,  $C_{15}H_7O_6Ag_3$ , forms a heavy white precipitate. When distilled with lime, the acid yields diphenyl.

*Fluorenedicarboxylic acid* is formed by the action of sodium amalgam on diphenyleneketonecarboxylic acid. It gives a *silver* salt of the formula  $C_{15}H_9Ag_2O_4$ , and yields fluorene when distilled with lime and a little zinc-dust.

A. J. G.

**Naringin.** By W. WILL (*Ber.*, 18, 1311—1325).—Analytical results obtained from naringin, and the properties of the substance, point to the probability of its being *methylnesperidin*,  $C_{23}H_{22}O_{12}$ , and not  $C_{23}H_{26}O_{12}$ , the formula assigned to it by Hofmann (*Abstr.*, 1879, 468). When heated with dilute acids, it yields isodulcitol and *naringenin*.

*Naringenin*,  $C_{17}H_{14}O_6$  ( $= C_{23}H_{26}O_{12} - C_6H_{14}O_6$ ), forms colourless lustrous needles without smell or taste, melting with decomposition at about  $230^\circ$ . It dissolves readily in alkalis, and is precipitated again

by acids and by carbonic anhydride. It is readily soluble in alcohol, ether, and benzene. In all its reactions, it resembles hesperidin. When boiled for 5—6 hours with aqueous potash, it splits up into phloroglucinol and *naringenic acid*,  $C_{11}H_{10}O_4$ . The latter compound melts at  $207^\circ$ ; it is insoluble in light petroleum, sparingly soluble in benzene and in cold water, more soluble in hot water, and readily in alcohol and ether. It gives a yellowish-red colour with ferric chloride. When heated with methyl iodide, potash, and methyl alcohol, it yields *methylic methylnaringenate*,  $C_{13}H_{14}O_4$ , crystallising in lustrous plates melting at  $68^\circ$ . By boiling this methyl salt with potash, the potassium salt of an acid (methylnaringenic acid?) is formed, which when acidified yields an acid melting at  $169^\circ$ . This acid gives no colour with ferric chloride; when reduced, it yields a hydro-acid melting at  $127^\circ$ . N. H. M.

**Quassin.** By V. OLIVERI and A. DENARO (*Gazzetta*, 15, 6—8).—The authors, in continuation of their investigations on quassin,  $C_{38}H_{44}O_{10}$  (Abstr., 1884, 1192), point out that by heating it in a current of dry air at  $150^\circ$  it can be converted with loss of 1 mol.  $H_2O$  into an anhydride, *quasside*,  $C_{32}H_{42}O_8$ . If heated with acetic anhydride and sodium acetate, however, 2 mols.  $H_2O$  are removed, with formation of a second anhydride,  $C_{32}H_{40}O_8$ , which forms a white pearl-like amorphous mass, soluble in alcohol, chloroform, and ether, and melts at  $150$ — $158^\circ$ . Phosphorus pentachloride reacts violently with quassin to yield a *pentachloro-derivative*,  $C_{32}H_{38}O_8Cl_5$ , a yellow powder, melting with decomposition at  $119^\circ$ ; it is probably derived from quassin by the substitution of two hydroxyl groupings and three hydrogen-atoms by chlorine. V. H. V.

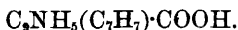
**Brazilin.** By K. BUCHKA and A. ERCK (*Ber.*, 18, 1138—1142).—The authors confirm Liebermann and Burg's description of *tetracetobrazilin* (this Journal, 1877, ii, 193). *Triacetobrazilin*,  $C_{16}H_{11}O_5\bar{Ac}_3$ , is obtained by heating brazilin for from 5 to 10 minutes with acetic anhydride in a reflux apparatus. It crystallises from alcohol in fine colourless needles, and melts at  $105$ — $106^\circ$ . By saponifying monobromotetracetobrazilin (*Ber.*, 17, 685) with barium hydroxide, *monobromobrazilin*,  $C_{16}H_{13}BrO_5$ , is obtained. It forms lustrous red plates, and becomes anhydrous and amorphous at  $100^\circ$ . By acting on tetracetobrazilin with excess of bromine vapour, and treating the product with sulphurous acid, *tribromotetracetobrazilin*,  $C_{16}H_7Br_3O_5\bar{Ac}_4$ , is obtained. It forms small white needles, melts at  $145$ — $147^\circ$ , and is readily oxidised in the air under the action of light. By acting on brazilin with excess of bromine vapour, and subsequently treating with sulphurous acid, *tetrabromobrazilin*,  $C_{16}H_{10}Br_4O_5$ , is obtained in slender pale-red needles. It dissolves in alkalis, yielding a transient violet colour, and on fusion with sodium acetate and acetic chloride yields *tetrabromotetracetobrazilin*,  $C_{16}H_8Br_4O_5\bar{Ac}_4$ ; this melts at  $220$ — $222^\circ$ . The authors have prepared pure brazilin by dissolving brazilin in the smallest possible quantity of alcohol, adding an excess of ether, and treating this solution in the cold with a small quantity of concentrated nitric acid for about six hours. A. P.

**Quinoline.** By A. CLAUS (*Ber.*, **18**, 1305—1311).—By the action of halogens on the halogen-alkyl-derivatives of quinoline, the following compounds were prepared:—*Bromobenzylquinoline dibromide*,  $C_9H_7N \cdot C_7H_7Br_2$ , crystallises from chloroform in large lustrous orange-red prisms. Its solution in alcohol by long heating gives up bromine, leaving quinolinebenzyl bromide. It melts at  $100^\circ$  (uncorr.). The corresponding *diiodide* forms dark violet needles melting at  $109$ — $110^\circ$  (uncorr.). It can be recrystallised from alcohol without decomposition, but gives off iodine if boiled with water. The *dichloride* forms long thin yellow needles melting at  $80^\circ$  (uncorr.). From quinoline benzylchloride a *dibromide* was obtained; it forms bright orange-yellow crystals melting at  $91$ — $92^\circ$  (uncorr.).

Quinolinecarboxylic acid also unites with halogens. *Cinchonic acid dibromide*,  $C_9H_8N \cdot COOH \cdot Br_2$ , forms long red needles melting at  $188^\circ$  (uncorr.). By boiling with water, it gives up all its bromine. On acidifying a solution of the dibromide in dilute soda, a part is recovered unchanged. *Cinchonic acid diiodide* forms green needles having a metallic lustre; it crystallises from alcohol in steel-blue plates. It begins to lose iodine at  $200^\circ$ , and at  $242^\circ$  it melts with decomposition. It is more stable than the dibromide. Halogen-additive products of the additive compound of quinolinecarboxylic acid with benzyl bromide, and of quinolinebenzylbetain were obtained.

The author describes a reaction by which alkyl-derivatives of quinoline can be distinguished from ammonium hydroxides. By the action of barium cyanide on quinoline ethylsulphate, for example, no stable cyanide is obtained; the cyanide of an ammonium base, on the other hand, is stable.

The acid obtained by Claus and Michael (*Abstr.*, 1884, 560), by the action of soda upon quinolinebenzylbetain, has been further examined, and found to be *benzylquinolinecarboxylic acid*,



It forms long, yellow, lustrous needles melting at  $218^\circ$ . It does not yield salts with acids. N. H. M.

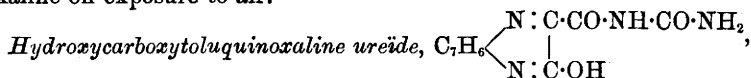
**Nitro- and Amido-derivatives of Quinoline.** By A. CLAUS and T. KRAMER (*Ber.*, **18**, 1243—1251).—By nitrating quinoline in the way described by Königs (*Abstr.*, 1879, 540) for the preparation of orthonitroquinoline, the authors obtained, besides orthonitroquinoline, a new mononitro-compound, probably metanitroquinoline, and two dinitro-derivatives, described as  $\alpha$ - and  $\beta$ -dinitroquinoline. The latter compound is alone formed when a higher temperature or a larger quantity of the nitrating mixture is employed. *Metanitroquinoline*,  $C_9NH_5NO_2$ , dissolves sparingly in water, crystallises in long slender lustrous needles, melting at  $72^\circ$ , and containing water of crystallisation.  $\alpha$ -*Dinitroquinoline*,  $C_9NH_5(NO_2)_2$ , is very sparingly soluble in water, dilute acids, benzene, and ether; readily in chloroform and concentrated acids. It forms lustrous, colourless needles, melting at  $182$ — $183^\circ$  (uncorr.), and sublimes unchanged. It dissolves in soda when warmed, with intense red coloration. When added to fused

potash, it detonates, and gives off ammonia; the residue contains potassium cyanide. By oxidation, it yields pyridinecarboxylic acid; the two nitro-groups are, therefore, in the benzene-ring.  $\alpha$ -Dinitroquinoline can be obtained by nitrating orthonitroquinoline, but no  $\beta$ -dinitroquinoline is formed in the reaction. The *hydrochloride* and *platinochloride* of  $\alpha$ -dinitroquinoline were prepared; they are very unstable.  $\alpha$ -Diamidoquinoline forms thick yellowish needles, which melt at  $156^\circ$  (uncorr.); it does not sublime without decomposition.  $\beta$ -Dinitroquinoline dissolves in boiling water and dilute acids more readily than the  $\alpha$ -compound; it is very readily soluble in hot alcohol and in chloroform. It forms dazzling white microscopic needles, melts at  $133$ – $134^\circ$  (uncorr.), and does not sublime without decomposition. When added to fused potash, it yields ammonia and potassium cyanide, but does not detonate. Its *hydrochloride* is more stable than that of the  $\alpha$ -compound; it is, however, decomposed by water, or by heating at  $100^\circ$ . The *platinochloride* forms lustrous bright yellow plates.  $\beta$ -Diamidoquinoline,  $C_9H_6(NH_2)_2$ , forms small yellow needles, melts at  $162$ – $163^\circ$ , and is readily soluble in water and alcohol, very sparingly in light petroleum and chloroform. Its *platinochloride* is described.

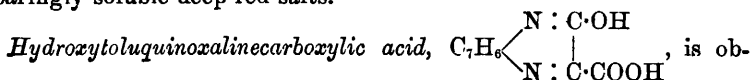
By heating dihydroxynitroquinoline, a sublimate of a mononitroquinoline was obtained; it melts at  $149^\circ$  (uncorr.), and resembles the mononitroquinoline described in this paper. N. H. M.

**Quinoxalines II.** By O. HINSBERG (*Ber.*, 18, 1228–1234) (compare *Abstr.*, 1884, 1052). — *Hydroxyphenyltoluinoxaline*,  $C_7H_6 < \begin{smallmatrix} N = CPh \\ N : C(OH) \end{smallmatrix} >$ , is obtained by the action of toluylenediamine on phenylglyoxylic acid. It forms pale-yellow hair-like needles, melts at  $196$ – $197^\circ$ , can be sublimed, and resembles hydroxymethyltoluinoxaline in properties.

$\beta$ -Naphthylenetoluinoxaline,  $C_{17}H_{12}N_2$ , is prepared by mixing at  $0^\circ$  solutions of  $\beta$ -naphthaquinone and toluylenediamine in acetic acid; it forms pale-yellow crystals, melts at  $139$ – $141^\circ$ , can be distilled, is insoluble in water, moderately soluble in alcohol, readily soluble in chloroform and benzene. By the action of stannous chloride on a solution of the base in hydrochloric acid, the hydrochloride of a new base is precipitated in brownish-black needles, which dissolve in water with a violet colour. The free base prepared from this is very unstable, and appears to be reconverted into naphthylenetoluinoxaline on exposure to air.



is obtained on mixing aqueous solutions of alloxan and toluylenediamine; it crystallises in deep yellow needles, which turn brown at  $250^\circ$ , and melt to a brown liquid at  $258^\circ$ . It is sparingly soluble in water and alcohol, and when treated with concentrated acids, yields sparingly soluble deep red salts.



tained from the ureide by boiling with aqueous potash, it crystallises in yellow plates or needles, is sparingly soluble in water, more readily in alcohol, gives red salts with acids, and colourless salts with bases; its aqueous solution gives a red coloration with ferric chloride. When heated at  $214^{\circ}$ , carbonic anhydride is eliminated, and *hydroxytoluinoxalinaline*,  $C_6H_4 \left\langle \begin{smallmatrix} N=CH \\ N:C(OH) \end{smallmatrix} \right\rangle$ , is formed. This crystallises in white needles, melts at  $241-242^{\circ}$  to a brown liquid, and is readily soluble in water and alcohol, scarcely soluble in benzene and ether.

*Toluinoxalinedicarboxylic acid*,  $C_7H_6 \left\langle \begin{smallmatrix} N:C(COOH) \\ N:C(COOH) \end{smallmatrix} \right\rangle$ , is prepared by adding toluylenediamine, as long as it is dissolved, to an aqueous solution of sodium dioxytartrate, heating to boiling for a short time, and then saturating with hydrochloric acid. It crystallises with  $\frac{1}{2}$  mol.  $H_2O$  in white needles or prisms, is readily soluble in water, alcohol, and ether, sparingly soluble in benzene, and when heated at  $145^{\circ}$  loses carbonic anhydride with formation of a solid acid, probably a toluinoxalinenemonocarboxylic acid. Stannous chloride acts on the dicarboxylic acid with formation of a reduction-product crystallising in greenish-black needles. The same substance is formed in small quantity by the action of toluylenediamine and dilute sulphuric acid on sodium dioxytartrate.

By the action of toluylenediamine on glyoxylic acid, no condensation-product was obtained, but by substituting the calcium salt for the free acid, and decomposing the precipitated salt with hydrochloric acid, an acid of the formula  $C_6H_6N_2O_2 + \frac{1}{2}H_2O$  was obtained; it crystallises in slender white needles, and is decomposed at  $160^{\circ}$ , with evolution of carbonic anhydride.

A. J. G.

**Cinchona Alkaloids.** By W. T. COMSTOCK and W. KÖNIGS (*Ber.*, 18, 1219—1227). Cinchine (Abstr., 1884, 1382) crystallises in the rhombic system,  $a : b : c = 0.6017 : 1 : 0.5022$ . *Cinchine methiodide*,  $C_{19}H_{20}N_2 \cdot MeI$ , crystallises in colourless monosymmetric forms  $a : b : c = 1.5838 : 1 : 0.9114$ .  $\beta = 84^{\circ} 11.5'$ . It melts at  $186^{\circ}$ , is sparingly soluble in water and ether, readily soluble in hot alcohol and dilute acids. When treated with silver oxide, the hydroxide seems to be formed, but could not be isolated. When shaken with silver chloride, and mixed with platonic chloride, it yields a platinochloride,  $C_{19}H_{20}N_2 \cdot HMePtCl_6$ , crystallising in lustrous, reddish-yellow feathery forms.

*Quinidine chloride*,  $C_{20}H_{23}N_2OCl$ , is prepared by heating quinidine hydrochloride with phosphoric chloride and chloroform, it crystallises well, melts at  $131-132^{\circ}$ , and is readily soluble in alcohol, benzene, and chloroform, sparingly in ether and light petroleum. When heated with alcoholic potash, it yields a base,  $C_{20}H_{22}N_2O$ , which proved to be identical with chinine (*loc. cit.*) Chinine crystallises in the rhombic system,  $a : b : c = 0.5322 : 1 : 0.6642$ . The zincchloride,  $C_{20}H_{22}N_2O \cdot H_2ZnCl_4 + 2H_2O$ , crystallises in rhombic prisms,  $a : b : c = 0.3424 : 1 : 0.4964$ . When heated with hydrochloric acid (sp. gr. 1.125) chinine yields a methochloride and a base not yet further investigated.

*Apochinine*,  $C_{18}H_{17}NO_2$ , is obtained as hydrobromide by heating chinine with hydrobromic acid (sp. gr. 1.49) at  $180^\circ$  for 6—8 hours. The free base is colourless and crystalline, melts at  $246^\circ$ , and is sparingly soluble in water, benzene, ether, and chloroform, readily soluble in alcohol. The hydrobromide forms yellow crystals. The mother-liquors contain a second bromine-free base, melting at  $177$ — $178^\circ$ . A. J. G.

**Strychnine and Brucine.** By H. BECKURTS (*Ber.*, **18**, 1235—1238).—Bromostrychnine and its hydrochloride, bromide, nitrate, and sulphate are described. The *methiodide*,  $C_{21}H_{21}BrN_2O_2 \cdot MeI$ , forms nacreous plates insoluble in ether, chloroform, and light petroleum, sparingly soluble in water, readily in dilute alcohol; when treated with moist silver oxide, it yields the *hydroxide*, which crystallises with 1 mol.  $H_2O$ , decomposes at  $265^\circ$  without melting, and is readily soluble in water.

*Dibromostrychnine*,  $C_{21}H_{20}Br_2N_2O_2$ , crystallises in hard rhombic tables, readily soluble in chloroform, benzene, and dilute alcohol, sparingly in water. It does not give any coloration with chromic mixture. The hydrochloride,  $C_{21}H_{20}Br_2O_2N_2 \cdot HCl$ , crystallises in needles. When boiled with water, the free base loses hydrogen bromide, and is converted into a base,  $C_{21}H_{19}BrN_2O_2$  (?), crystallising in needles, and melting at  $216^\circ$ .

The other results obtained by the author with the bromostrychnines are identical with those obtained by Shenstone (*Trans.*, 1885, 139); the author, however, claims priority for his work, it having been described in 1884, and published in abstract in *Chemiker Zeitung*, 1884, Parts 79, 82).

A tribromo-compound is obtained as a yellow precipitate by the action of bromine-water on brucine hydrobromide; it is very probably brucine dibromide hydrobromide,  $C_{23}H_{26}N_2O_4Br_2 \cdot HBr$ . A. J. G.

**Aconitine.** By K. F. MANDELIN (*Arch. Pharm.* [3], **23**, 161—177).—A sample of japaconitine, obtained from Merck, was found by the author to agree exactly in its chemical and physiological behaviour with aconitine. From this, the author infers that the two substances are identical, and he considers that the chief point of difference insisted upon by Wright and Luff, that japaconitine gives no apoderivative, is not to be relied on, as it rests on the estimation of a very small quantity of water. Langgaard's figures of the comparative toxic powers of japaconitine and aconitine are also no criterion, as the *dosis letalis* he quotes for the latter is much too high, while the figures he gives for the former agree in the main with those obtained by the author for aconitine.

The author has also been unable to detect any difference between pseudaconine and aconine; the differences observed by Wright and Luff he attributes to the presence of undecomposed pseudaconitine in the preparation of pseudaconine. The aconitines are thus analogous to the tropines.

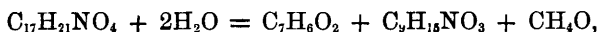
The old tests for aconitine are described by the author as worthless. Pure aconitine should give a colourless solution in concentrated

sulphuric acid, which should not be darkened by the addition of a few drops of strong sugar solution. This substance is also precipitated in very dilute solutions by mercuric bromide, picric acid, and other reagents, whilst aconine is only thrown down in stronger solutions. Pseudoaconitine may be recognised by its yielding protocathechuic acid when treated with potash, by its reaction with fuming nitric acid and alcoholic potash, and by its behaviour with sulphovanadic acid. Evaporated on a watch-glass, with a little fuming nitric acid, a yellow residue is obtained, which gives a purple-red coloration on addition of alcoholic potash. A solution of pseudoaconitine in strong sulphuric acid yields a violet coloration with sulphovanadic acid. With all these reagents, aconitine gives negative results.

About 3 mgrms. of aconitine would be sufficient to kill a man, whilst as a medicinal dose not more than 0.1 mgrm. should be taken at once. The author recommends the pharmacodynamic method as the best one for estimating the strength of an aconitine preparation.

In conclusion, the author states that the alkaloids acolyctine and lycoctonine, obtained by Hubschmann from *A. lycoctonum*, are not identical with aconitine and pseudoaconitine. J. K. C.

**Constitution of Cocaine.** By G. CALMELS and E. GOSSIN (*Compt. rend.*, 100, 1143—1146).—Cocaine platinochloride has the formula  $(C_{17}H_{22}NO_3Cl)_2PtCl_4$ . When the hydrochloride is heated with water and baryta in sealed tubes at 120°, it splits up in accordance with Lossen's equation—



the actual products being methyl alcohol, barium benzoate, and a compound of barium benzoate and the barium salt of ecgonine, which forms slender prismatic needles, very soluble in water and alcohol, only slightly soluble in ether.

This double compound forms a convenient source of ecgonine. Ecgonine platinochloride,  $(C_9H_{15}NO_3Cl)_2PtCl_4$ , is extremely soluble in water, but much less soluble in alcohol, provided the latter does not contain platinum tetrachloride. It is obtained as a yellow powder by precipitating it in absolute alcohol, or in red prisms by adding alcohol to the aqueous solution. A modified salt,  $(C_9H_{15}NO_3)_2PtCl_4$ , is obtained by heating solutions of the preceding compound. It forms yellowish needles, very soluble in water, but almost insoluble in alcohol, even in presence of platinum tetrachloride. Ecgonine aurochloride is a greenish-yellow gummy compound, very soluble in water and alcohol. The hydrochloride forms a yellow confusedly crystalline mass, very soluble in water and alcohol. Ecgonine has a neutral reaction, but combines with alkalis to form gummy compounds, which are very soluble in water and in alcohol, and crystallise with great difficulty. They have a faintly alkaline reaction.

When ecgonine is heated with moderately strong sulphuric acid, neither carbonic oxide nor formic acid is formed, but an alkaloid is obtained, which stands in the same relation to ecgonine as ether to alcohol. It forms a barium salt of the composition  $C_{18}H_{22}N_2O_5Ba$ , and



its basic or acid salts are less soluble and crystallise more readily than those of ecgonine. The hydrochloride crystallises in stellate groups of prismatic needles, and the platinochloride forms feathery groups of large crystals, very soluble in water and in alcohol.

When the double barium compound obtained by the action of baryta on cocaine is subjected to destructive distillation, it yields an isotropine, the hydrochloride of which has the composition  $(C_8H_{15}NO)_2 \cdot H_2PtCl_6$ , and forms bulky orange-red deliquescent crystals.

It would seem that cocaine, ecgonine, and isotropine are derivatives of ethyl tetrahydropyridine: isotropine is methoxyethyltetrahydropyridine, ecgonine is methoxyethyltetrahydropyridinecarboxylic acid, cocaine is methyl benzomethoxyethyltetrahydropyridinecarboxylate.

C. H. B.

**Ptomaines.** By F. COPPOLA (*Gazzetta*, **14**, 571—572).—In a former memoir on the ptomaines the author has pointed out the probability that their genesis is due to the processes, such as Dragendorff's, used for their extraction (this vol., p. 278); a description is given of experiments on the putrefaction of large quantities of various tissues and organs, such as muscle, pancreas, spleen, brain of dog, &c., kept from free access of air, and at the ordinary temperature. For a fortnight, the putrefying mass had an acid, but at the end of six weeks a decidedly alkaline reaction. Both the liquid and the solid portions of the resultant mass were extracted with benzene. The extract, on evaporation, gave an abundant yellow residue, which showed all the characteristic reactions of alkaloids. From this result it is inferred that the process of putrefaction is not capable of producing ptomaines, but that the acid reaction conduces to the decomposition of lecithins with generation of a substance having the properties of an alkaloid.

The relatively small quantity obtained from more than 2 kilos. of putrefying material seems further to indicate that the alkaloids extracted by the Dragendorff and Stass-Otto methods are mainly formed by the processes employed for their extraction.

V. H. V.

**Behaviour of Serum Albumin towards Acids and Neutral Salts.** By J. E. JOHANSSON (*Zeit. physiol. Chem.*, **9**, 310—318).—The author's researches are a development of the results published by Hammarsten (this vol., p. 611). The conversion of this albumin into acid albuminate by digestion with dilute acids was first investigated with the following results:—

(a.) Duration of digestion, one month at ordinary temperatures, with 1 or 2 per cent. solution of acetic acid, or with 0.25 per cent. hydrochloric acid; no conversion. (b.) Duration various, with 0.5 per cent. hydrochloric acid; conversion first evident after 16 days, with 1 per cent. hydrochloric acid after 8 days. (c.) At the temperature of 40° with 0.25 per cent. hydrochloric acid, after 14 days.

On the other hand, the presence of 0.2 per cent. sodium hydroxide determined rapid conversion into albuminate, which was evident after the lapse of  $2\frac{1}{2}$  hours. In the latter case, the albumin lost nitrogen, in the form of ammonia, and sulphur.

Increasing the proportion of hydrochloric acid to 1, 2, and 3 per cent. respectively, the periods which elapsed before the conversion into

albuminate became evident were 8 days, 24 hours, and 5 hours respectively. In these experiments, the albumin solutions had been freed from salts by prolonged dialysis.

Corresponding experiments in which the solution was saturated with magnesium sulphate, proved that the presence of the salt considerably retarded the conversion.

The author bases the following method for the preparation of serum albumin on these observations. The serum is saturated with magnesium sulphate at 30°, allowed to cool, filtered, and the albumin then precipitated by adding acetic acid. The precipitate is redissolved and again precipitated by acetic acid in presence of magnesium sulphate. It is then redissolved in water, and the solution, after neutralising, submitted to dialysis. Finally the albumin is separated by precipitation with alcohol.

C. F. C

### The Sulphur of Casein and the Determination of Sulphur in Proteids. By O. HAMMARSTEN (*Zeit. physiol. Chem.*, 9, 273—309).

—The investigations detailed in this paper were undertaken in consequence of Danilewsky's criticisms (*ibid.*, 7) on the results, previously published by the author, of the determination of sulphur in casein, the mean of several concordant analyses having given the percentage number 0.716. After a critical discussion of the results of other observers, as bearing on the strictures of Danilewsky, and of the probable errors attaching to the various methods hitherto proposed for the determination of sulphur in organic compounds, including the error common to all occasioned by the slight solubility of barium sulphate, the author details the results of the experimental investigation of six of these, as applied to the analysis of one and the same preparation both of casein and other proteids. These methods are, as regards their essential differences, as follows:—

1. (a) Liebig's method, consisting of fusion with potassium hydroxide and nitrate; and (b) the more commonly-adopted modification which consists in first mixing the substance with sodium carbonate and potassium nitrate, and adding this in small portions at a time to the before-mentioned mixture kept in a state of fusion.
2. The modified method previously employed by the author (*ibid.*, 7), which consists essentially in the destruction of the organic molecule by digestion with nitric acid prior to the alkaline nitrate fusion.
3. Loew's method (*Pflüger's Archiv*, 31, 394), which consists in fusing with 20 parts of a mixture of sodium carbonate (4 parts) and potassium chlorate (1 part).
4. Claesson's method (*Zeit. anal. Chem.*, 22, 177), in which the substance is burnt in a stream of oxygen and nitric oxide.
5. The Mixter-Sauer combustion method (*Zeit. anal. Chem.*, 22, 581). In all cases the results (percentages) of the analyses are calculated on the ash-free substance, which was dried at 110—115° previously to weighing. The following are the experimental results:—

*Casein I.*—Prepared from milk by Radenhausen and Danilewsky's method, namely, by dilution and precipitation with hydrochloric acid, re-solution of the precipitate in ammonia, reprecipitation by hydrochloric acid, and washing with water, alcohol, and ether:—

Method—	1a.	1b.	2.	3.	4.	5.
	—	0·672	0·798	—	—	—
	0·773	0·667	0·789	0·726	0·701	0·780

*Casein II.*—Prepared by the author's method of thrice precipitating by acetic acid. The ash amounted to 0·21 per cent.

Method—	1a.	1b.	2.	3.	4.	5.
	—	0·598	—	—	—	—
	0·775	0·618	0·778	0·731	0·729	0·747

*Casein III.*—As in the preceding, but four times precipitated (ash = 0·109 per cent.).

Method—	1a.	1b.	2.	3.	4.	5.
	0·758	0·628	—	—	—	—
	0·769	0·667	0·774	0·729	0·763	0·730

*Casein IV.*—Prepared as in I (ash = 0·25 per cent.).

Method—	1a.	1b.	2.	3.	4.	5.
	—	—	—	—	0·763	—
	0·774	0·681	0·774	—	0·766	0·759

The mean results with the four preparations are as follows :—

Method—	1a.	1b.	2.	3.	4.	5.
	0·770	0·647	0·783	0·729	0·755	0·754

The mean result of these analyses is 0·758 per cent., which number is identical with that previously published by the author; Danilewsky's objections, therefore, fall to the ground. The high percentage, exceeding 1 per cent., obtained by him, is probably accounted for by the presence of impurities.

In conclusion, the author gives the results of an extension of his comparative investigation of the above analytical methods to other albuminoids.

*Egg albumin* was prepared from white of egg by separating the globulin by precipitation with acetic and carbonic acids, and heating the filtrate to boiling. It is not, therefore, to be regarded as a pure albumin. It contained 0·56 per cent. ash.

Method—	1a.	1b.	2.	4.	5.
	—	1·52	—	—	—
	—	1·54	1·70	—	—
	1·67	1·34	1·65	1·62	1·58

Here, as in the analysis of the casein, the highest numbers are obtained with 1a and 2.

*Gelatin.*—The preparation analysed was a fine gelatin of commerce containing 1·74 per cent. ash. The following are the percentage numbers obtained :—

Method—	1a.	1b.	2.	4.	5.
	0·718	0·680	0·747	0·746	0·665

Of these methods, therefore, 1a and 2 appear the most trustworthy; and of these two selected by the author, the latter, being more troublesome, is to be preferred only in cases where the percentage of sulphur in the substance to be analysed is presumably low. The combustion methods 4 and 5 are sufficiently trustworthy to be employed in cases where such a method may be, from other considerations, advantageously employed.

C. F. C.

**Amido-acids resulting from the Action of Hydrochloric Acid and of Barium Hydroxide Solutions on Albuminoids.**

By E. SCHULZE (*Zeit. physiol. Chem.*, 9, 253—259).—The amido-acids resulting from the decomposition of conglutin by the above reagents are, in the case of the former, optically active, in the case of the latter optically inactive. Of these, the author finds that the hydrochloride of the inactive glutamic acid is identical in crystalline form with the hydrochloride of the ordinary optically active acid.

In regard to the solubility of optically active leucine, the author confirms his previous statements (*ibid.*, 63—126), namely, 1 in 40 parts of water at ordinary temperatures. Preparations of leucine from various sources and variously crystallised gave numbers within the limits—1 in 40 and 1 in 45 parts water, according to the temperature of solution.

The solubility of glutamic acid (inactive) has also been reinvestigated, the numbers obtained varying between 1 : 59 and 1 : 61 parts water as compared with 1 : 45 previously given (*loc. cit.*).

In conclusion, the author furnishes a number of corrections of previous communications.

C. F. C.

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### Physiological Chemistry.

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**Digestion of Cellulose by the Horse.** By V. HOFMEISTER (*Bied. Centr.*, 1885, 254—257).—Various forms of cellulose, such as that of hay and oats, of paper, &c., were submitted to the action of a phenol water extract of the gastric glands, and of the fresh mucous membrane of the duodenum and cæcum of the horse; the results were negative, but the fresh intestinal juices dissolved 40—78 per cent., whilst the juices when boiled were inactive; the amount of solution depended on the time allowed for solution, but no increase was obtained by permitting the fluids to be in contact with cellulose longer than they would be naturally in the horse. The presence of alkaline carbonates, bacteria, &c., has no influence on solution, but a temperature of 100° is absolutely fatal. Apparently the decomposition products of cellulose are of a gaseous nature. E. W. P.

**Assimilation of Cellulose.** By W. v. KNIEREM (*Zeit. f. Biol.*, 21, 67—139).—Haubner, who was the first to determine the amount of

cellulose digested by oxen, and all subsequent observers used a method of research which is open to objection if the research is of any duration. They simply determined the difference between the amount of cellulose ingested with food and that found in the fæces, assuming that the residual contents of the intestine remained constant both in quantity and composition during the experiment. This may lead to serious error in the case of herbivores, considering the length of intestine and the slow excretion of fæcal matter. In the present experiments this source of error has been eliminated by freeing the intestine of the research animal from cellulose by means of a cellulose-free diet, then giving a known quantity of cellulose, and finally determining the daily elimination till the intestine is again free.

Experiments were made as to the digestibility and food value of cellulose with men, dogs, fowls, and rabbits. No difficulty was experienced in the three first cases in freeing the alimentary canal of cellulose by giving an exclusively cellulose-free diet. With rabbits, on the other hand, this difficulty had to be contended with. After a few days' feeding on a purely animal diet, they gradually sank and died. On post-mortem examination the cause of death was found to be stoppage of the cæcum. With the relatively long intestine and slow passage of the intestinal contents, the danger of such a stoppage is very great. It is the cellulose which gives the loose consistency to the intestinal contents which ensures their safe passage. Cellulose is essential, therefore, in the case of herbivores, to produce this mechanical effect. Horn shavings were also found to possess this mechanical effect, and they, moreover, had the further recommendation that they passed through the organism without any change. By their agency the rabbit's intestine was freed from cellulose.

Henneberg's method was used for determining the amount of cellulose both in food and fæces. It consists in extracting, first with weak acid, then with weak alkali, and finally with ether-alcohol. In the separation of the cellulose the author has used a centrifugal machine with advantage; the cellulose soon separates and can be filtered with ease.

Men, whose alimentary canal had been freed from cellulose by nine days' animal food, digested only 4.4 per cent. of the cellulose of *Scorzonera Hispanica* and 25.3 per cent. of that of lettuce leaves. Fowls were incapable of digesting cellulose in any of the following forms:—Wadding, paper, rye-straw, or cabbage, and the same negative result was obtained when grass, wadding, or linen, were given to a dog. Rabbits digested 5 per cent. of the hard cellulose of the outer shell of the stone fruit, 20.5 per cent. of the cellulose of sawdust, 25.4 per cent. of that of cabbage, 52.5 per cent. of that of hay, 54.4 per cent. of that of paper, and 65.3 per cent. of that of carrot meal.

The undigested cellulose separated from the fæces in the hay experiment was again given to a rabbit, and the undigested cellulose in this second experiment was given a third time to another animal in order to determine whether any difference existed between the digestibility of the residue. The same sample of cellulose passed through the organism three separate times; the first time 52.5 per cent. was

digested, the second time, 40·8, and the third time only 20 per cent. The residue, therefore, remaining undigested becomes more difficult of assimilation each time it passes through. Systematic experiments were also made on the consumption of proteïd and fat with and without the presence of cellulose. The general result is that cellulose acts similarly to carbohydrates, that is, it economises the metabolism of proteïd and fat. With reference to the process by which cellulose is dissolved, Tappeiner has shown that it takes place in the paunch and colon, and that it is not the result of an unorganised ferment, but of a fermentation produced by living organisms. This accounts for the fact that it only takes place in those parts of the intestine where there is long contact, and also that animals with relatively short intestines and quick digestion are unable to assimilate it, or if at all, only to a slight extent. For every 100 grams of cellulose dissolved, 43 grams of mixed gases are formed (38 per cent.  $\text{CO}_2$  and 5 per cent.  $\text{CH}_4$ ) and 57 grams of fatty acids (butyric and acetic). It is to the latter that the chief importance is to be attached, as the calorific value of 1 gram of a mixture of equal parts of butyric and acetic acids is greater than the calorific value of 1 gram of either starch or cellulose.

J. P. L.

**New Method of Proximate Resolution of the Brain Substance.** By F. BAUMSTARK (*Zeit. physiol. Chem.*, 9 145—210).—The basis of the author's method consists in a development of the observation made by Couerbe (*Annalen*, 13, 222) that the action of ether on the fresh brain substance is confined in the first instance to a displacement of its water. Dialytic experiments in which carefully prepared animal membranes (portions of intestine) were employed as the septum, established the following diffusion phenomena:—(1.) Water diffuses into ether. The diffusion is increased by the addition of alcohol. (2.) Water diffuses into benzene and into light petroleum, to which a certain proportion of alcohol has been added; otherwise no diffusion takes place. The phenomena are evidently correlated with those of reciprocal solution: at the same time the water (or aqueous solution) diffuses in quantity much in excess of the solvent capacity of the several solutions, in which consequently it collects as a distinct stratum; it is also remarkable that the diffusion always sets from the water to the ether or benzene-alcohol, and never in the opposite direction. The application of these results to the proximate resolution of the complex brain substance has been carried out by the author in the most exhaustive manner. The following table exhibits the analytical numbers obtained with both the white and grey substance of the brain (horse), for a complete account of which, as also of the method of analysis, the more elaborate tables of the original must be consulted.

From these numbers, the following comparisons are drawn:—

(1) The constituents soluble in water, namely the soluble salts, albumin, and organic extractive matters, vary with the percentage of water, that is, they are present in greater proportion in the grey substance; (2) the aggregates of ash and organic constituents are nearly identical in the white and grey; (3) as are also the nucleïn,





cholesterin (combined), and lecithin; (4) on the other hand, the white substance contains the larger proportion of neurokeratin, free cholesterin, and protagon; (5) whereas the grey substance exhibits a relative preponderance of insoluble albumin and connective tissue; (6) the distribution of phosphorus is exhibited by the following percentage numbers:—

	White.	Grey.
In the ash.....	0.0532	0.0554
„ protagon .....	0.0258	0.0111
„ ethereal extract ..	0.3115	0.2234
„ nucleïn .....	0.0081	0.0046

The aggregate percentage of phosphorus in the fresh brain is 0.347 or 1.297 of the anhydrous substance.

The well-defined separations which this method permits have enabled the author to throw light on many points which have been the subject of divergent opinions. He has isolated and studied the hitherto doubtful protagon in such a way as to establish its identity beyond all doubt. The analyses of this compound give results agreeing closely with those of Blankenhorn and Gamgee; the author's account of its physical properties is equally confirmatory of their observations.

In regard to the relationship of protagon to cerebrin and lecithin, it is clearly shown that the latter are united in the molecule of the former in the closest chemical union. The following are the more important points in the proof. (1.) The invariability of the physical properties of protagon, including its melting point, which, moreover, is higher than that of cerebrin. (2.) The absence of any hygroscopic tendency; lecithin, on the other hand, is extremely hygroscopic. (3.) The failure of such solvents as ether, in the cold, or alcohol of 85 per cent., at 40—45°, to resolve protagon, or to cause, by fractional separation, any variation in the percentage of the fractions from the original. In no case was the author able to detect cerebrin, in the free state, as a constituent of the brain substance. The "combined cholesterin," in the ethereal extract, appears to be in the form of an oleate. Not the least valuable portion of the paper is the author's critical discussion of the views of previous investigators of this complicated subject. His investigations are proceeding.

C. F. C.

**Peculiarities of the Chemical Composition of Contractile Tissues.** By C. F. W. KRUKENBERG and H. WAGNER (*Zeit. f. Biol.*, 12, 25—40).—The peculiar taste of many kinds of flesh is probably attributable to the presence of carnine, or some closely allied substance. A substance similar to carnine is described as having been obtained from the muscles of the frog, alligator, lobster, and certain fresh-water fish. Pure carnine is unaffected by long continued boiling with concentrated baryta-water, and it readily forms salts; it is, therefore, probably not simply an acetate of hypoxanthine, a view which is further supported by the fact that hypoxanthine does not combine with acetic acid. The authors find, contrary to previous observation,

that hypoxanthine does not decompose when exposed to temperatures under  $260^{\circ}$ . In the preparation of pure carnine from Liebig's extract of meat, two new and well-characterised substances were obtained. The first is prepared by the following method from the basic lead acetate precipitate, after washing it with hot water:—The precipitate is suspended in water, decomposed with sulphuretted hydrogen, and the filtrate after concentration is treated with three times its volume of alcohol, whereupon a white precipitate is formed free from inosite; this crystallises in nacreous plates from its aqueous solution, on the addition of hydrochloric acid. The second substance is a pigment insoluble in alcohol, ether, and bisulphide of carbon, slightly soluble in cold, soluble in hot water, to which it imparts a golden-yellow colour. A comparative analysis of the light and dark red muscles of salmon was made in order to determine whether any chemical difference existed corresponding with their great variation in colour. This was found not to be the case, the two analyses showing similar composition.

The authors point out the necessity of studying vital processes themselves, instead of isolating definite chemical bodies which are extravital, and decomposition-products of either living or dead tissue.

J. P. L.

**Examination of the Organs of Bojanus in Anodonta.** By A. B. GRIFFITHS and H. FELLOWS (*Chem. News*, 51, 241).—The authors consider that their experiments establish the renal functions of the organs of Bojanus of the fresh-water mussel.

D. A. L.

**Distribution of Ammonium Salts and Formation of Urea.** By W. SALOMON (*Bied. Centr.*, 1885, 280).—The blood of dogs, rabbits, and kine contains 2.2—4.9 mgrams. ammonia per 100 c.c.; 100 grams rabbit liver contain 7.0—11.8 mgrams.; 100 grams muscle of dog and rabbit 6.1—12.4 mgrams. The kidneys are not necessary for the change of the ammonium salts into carbamide, and in the herbivora the seat of change is the liver.

E. W. P.

**The Pepsin Ferment.** By C. SUNDBERG (*Zeit. physiol. Chem.*, 9, 319—322).—The author has examined the reactions of this substance in a solution prepared according to the following method:—The stomach of a calf was beaten up, with the addition of common salt, in a mortar, and sufficient water added to form a saturated solution with the salt. After allowing the solution to remain three days, it was drained away, slightly acidulated, and subjected to dialysis. The resulting solution, freed from salts, was then digested for 7—14 days at  $40^{\circ}$ , and the pepsin further purified by adding calcium chloride and precipitating the calcium as phosphate, collecting the precipitate and isolating the pepsin by redissolving in hydrochloric acid and dialysing the solution. The product, which was highly peptic, did not give any reaction with tannin, mercuric chloride, platinum chloride, or lead acetate. The only precipitant found by the author for the pepsin was alcohol. From these results, the author concludes that the pepsin ferment does not belong to the albuminoid group.

C. F. C.

**Albuminoids of Human Milk.** By F. BIEDERT (*Zeit. physiol. Chem.*, 9, 354—355).—A question of priority.

**Fate of Cystein and the Formation of Sulphuric Acid in the Animal Body.** By E. GOLDMANN (*Zeit. physiol. Chem.*, 9, 260—272).—The author's experimental investigation of this subject is based on the *a priori* conclusion that the evacuation of cystein in the urine will be attended by an alteration of the normal ratio of oxidised to unoxidised sulphur, the sulphur of cystein being presumed to be converted into sulphuric acid under normal bodily conditions. Preliminary observations of this normal ratio in the animals (dogs) employed gave numbers varying from 0·2 to 0·45. The mean ratio resulting from seven analyses of urine voided on successive days during which a uniform diet (2 lbs. of biscuit) was maintained, was 1 : 0·38. The animal then received 15 grams of chlorobenzene per diem, from which there was no apparent disturbance of digestion. The urine forthwith became lævogyrate, and gave the characteristic reactions of mercaptan acids: on acidification, chlorophenylmercaptic acid crystallised out. The following are the details of the analyses of the urine:—

Date. 1894.	Rotation.	Total urine.	Sp. gr.	Oxidised sulphur. (A.)	Unoxidised sulphur. (B.)	Total sulphur. (1.)	Ratio A : B.
13th Sept...	5°	340 c.c.	1·050	0·4552	0·3223	0·7775	1 : 0·78
14th " ..	4° 10'	290 "	1·040	0·1593	0·2599	0·4192	1 : 1·631
15th " ..	1 40	386 "	1·036	0·1352	0·2187	0·3539	1 : 1·617
16th " ..	—	222 "	1·037	0·0793	0·0884	0·1677	1 : 1·115
17th " ..	—	244 "	1·044	0·0955	0·1072	0·2027	1 : 1·122
18th " ..	—	240 "	1·045	0·2620	0·1320	0·3940	1 : 0·503
19th " ..	—	272 "	1·042	0·3110	0·1560	0·4670	1 : 0·501
20th " ..	—	314 "	1·043	0·2835	0·1413	0·4248	1 : 0·490
23rd " ..	—	222 "	1·047	0·2180	0·1170	0·3350	1 : 0·530

From these numbers, it will be seen that the ratio in question undergoes a rapid increase to four times the normal. The variations in the total sulphur from the normal mean (0·2871 gram) also deserve attention; the rapid increase on the first day shows a sudden influence on the albuminoids of the body. The lævorotary power of the urine is contemporaneous with the disturbance of the sulphur ratio: at the same time it progressively decreases. The quantity of sulphuric acid diminishes at first relatively, in the end also absolutely. From these facts, the author considers that the sulphur voided under these abnormal conditions in the form of substituted cysteins, is under normal conditions converted into sulphuric acid.

A second series of experiments entirely confirmed the results of the first. It was further found that by increasing the quantity of chlorobenzene exhibited, the ratio of unoxidised to oxidised sulphur could be increased to 3 : 1. A direct investigation of the fate of

cystein was then instituted, consisting in the addition of 2.02 grams per diem, in the form of the hydrochloride, to the ordinary diet. An analysis of the urine showed that the sulphur ratio was unaffected; moreover, no traces of cystein were voided. This result confirms the previous deductions.

In conclusion the author gives the results of the comparative analyses, in regard to the sulphur ratios, of urine in the fresh state, and after being allowed to ferment for five weeks:—

	Sp. gr.	Oxidised sulphur. (A.)	Unoxidised sulphur. (B.)	Total sulphur.	Ratio, A : B.
Fresh urine . . . . .	1.044	0.2280	0.0860	0.3140	1 : 0.38
After fermentation	1.044	0.1734	0.0866	0.2600	1 : 0.49

The unoxidised sulphur remained, therefore, totally unaffected, whence it may be concluded that the compounds of which it is a constituent are of a stable character. C. F. C.

**Histological Chemistry in Relation to the Physiology of the Kidney.** By H. DRESER (*Zeit. f. Biol.*, 21, 41—66).—In the following paper, which is for the most part of more histological than chemical importance, the author has determined—1st. What are the precise relations of the acid secretion? 2nd. Whether it is possible to prove directly by means of the secretion a consumption of oxygen by the gland-cells?

In order to determine the precise relations of acid secretion 5 to 10 per cent. solutions of acid magenta were injected into the dorsal lymph-sac, and the subsequent changes noted. The urine of the first few hours after the injection was of a deep red colour, and showed no change of colour-intensity on the addition of acid. The author points out that this property of the urine implies, that parallel with the secretion of the colouring matter a quantity of acid or of an acid salt is secreted which is equivalent to the same quantity of alkali which would render the urine colourless. 15 to 20 hours after the injection, the urine is less coloured, and shows a marked change in colour-intensity on the addition of acid. Addition of hydrogen peroxide or other oxidising agents simply act as diluents, so that the colour is rendered latent not by reduction, but by combination with alkali. After long intervals, the quantity of colouring matter suffers a gradual diminution, the total quantity in the urine being much less than at the commencement of the experiment.

By the aid of this colouring matter, it can be demonstrated, as Maly asserted, that it is possible to have an alkaline reacting solution, and at the same time acid reacting substances present.

The author considers the urine to consist of two components, the acid and the alkaline. The acid component originates from the tubuli contorti as borne out by microscopic observation, the alkaline component being the filtrate from the glomeruli. During unusual activity, the alkaline secretion preponderates.

A complete account is given also of all the microscopical observations. In determining the second question, solutions of  $\frac{1}{2}$  to 1 per

cent. of methylene-blue were injected. The urine secreted after these injections was almost colourless, and on shaking with air or on the addition of ferric chloride gave rise to an intense deep blue. The same reduction was observed with many other colouring matters—magenta, methyl-violet, and methyl-green—but if the sulphonic acids of these colours were injected they passed through unchanged. This property of the sulphonic acids has been previously demonstrated by Bowmann and Herter in their experiments with sodium phenyl-sulphonate.

J. P. L.

**Pathological Acid Occurring in the Urine of Diabetic Patients.** By E. STADELMANN (*Zeit. f. Biol.*, 21, 140—144).—The author objects to Minkowski's criticism of his former paper (*Archiv. F. Experiment Path.*, 17), in which he communicated the occurrence of  $\alpha$ -crotonic acid in the urine of diabetic patients, on the ground that the  $\alpha$ -crotonic acid may have been primarily present as such, and not formed as a decomposition product of hydroxybutyric acid.

A quantity of pure hydroxybutyric acid from the urine of a diabetic patient was subjected to distillation. At 100—102°, a watery distillate came over which had an acid reaction, and was found to contain  $\alpha$ -crotonic acid, so that the decomposition of the hydroxybutyric acid must take place even at so low a temperature as 100°. After a gradual rise of temperature, the contents of the retort boiled constantly at 183—184°, and the distillate, which crystallised on cooling, consisted of  $\alpha$ -crotonic acid.

J. P. L.

**The Copper-oxide-reducing Constituent of Normal Urine.** By M. FLUCKIGER (*Zeit. physiol. Chem.*, 9, 323—353).—This paper contains an elaborate discussion of evidence bearing on the identity of this substance, to which the author has also contributed a number of experimental results; of these the following are the more important. It is destroyed (disappears) in the evaporation of the urine at 90—100°, but is only partially affected by evaporation at low temperatures, such as 60°.

It is soluble in alcohol, insoluble in ether. It is partially precipitated by barium hydroxide and by lead acetate. In the process of isolating it, a considerable proportion is lost during the subsequent treatment of the lead precipitate. In addition to its power of reducing cupric oxide in alkaline solution, it possesses that of holding the resulting cuprous oxide in solution. It is a dialyte. It yields acetone on oxidation with chromic mixture. The author's results are generalised into the hypothesis that the reducing constituent in question is a compound of glycuronic acid with a nitrogenous product of metabolism. This hypothesis is in harmony with the observation of the presence of acetone in diabetic urine, which probably also contains glycuronic acid, and with the evidence afforded by the study of acetonuria. It was also confirmed by the direct investigation of the oxidation of glycuronic acid.

C. F. C.

**Composition of Horse's Urine.** By E. SALKOWSKI (*Zeit. physiol. Chem.*, 9, 241—245).—The author gives the details of the

method and the results of the analysis of the urine of a horse in normal condition, fed upon 2 kilos. oats, 2 kilos. hay, 1 kilo. bran per diem, together with a small quantity of chaff. The quantity of urine voided in 48 hours was 410 c.c., of sp. gr. 1·046. The following table exhibits the quantities of the constituents estimated. (A) For 100 c.c. urine. (B) For the aggregate of 24 hours :—

Water.....	87·920	1806·760	
Dry residue .....	12·080	248·240	
Organic matter .....	9·638	198·061	
Inorganic matter .....	2·442	50·183	
Total nitrogen .....	3·092	65·340	
Ammonia .....	0·018	0·357	
Uric acid .....	traces	—	
Hippuric acid .....	0·759	15·597	
SO <sub>3</sub> .....	0·472	10·229	} 13·464
Sulphur in organic compounds (as SO <sub>3</sub> ).....	0·154	3·165	
P <sub>2</sub> O <sub>5</sub> .....	0·011	0·220	
CaO .....	0·278	5·713	
Sodium chloride .....	1·320	27·126	
Phenol .....	0·119	2·415	
Sulphur as SO <sub>3</sub> .....	0·189	4·068	} 5·136
Sulphur unoxidised in com- bination .....	0·062	1·268	

Ammonia, although not quite absent as in rabbit's urine, is present in very much less quantity than in human urine, relatively to the total nitrogen. The ratio of N as NH<sub>3</sub> : total N = 1 : 214.

The ratio of "neutral" to oxidised S = 1 : 3·2, which is approximately that of rabbit's urine : it is higher than in human urine (1 : 6). The ratio total S : total N = 1 : 12·3, is also higher than in human urine (1 : 15·6). Calcium is present in relatively large quantity (CaO : N = 11 : 1·4), and is in combination chiefly as sulphate.

C. F. C.

**Physiological Action of Trimethylhydroxyethyl- and Trimethylvinyl-ammonium Hydroxides.** By V. CERVELLO (*Gazzetta*, 15, 4—5).—As the neurine of commerce consists of a mixture in various proportions of trimethylhydroxyethyl- and trimethylvinyl-ammonium hydroxides, the author has studied separately the physiological action of each of these substances prepared by artificial methods. Both produce dilatation of the pupil and suspension of respiration with complete paralysis, but the hydroxyethyl base produces the more marked effect.

As regards the antagonism between neurine and atropine, it is found that the latter overcomes the effect of the former on the heart and glandular system ; but, if the dose is mortal, does not prevent death. These facts tend to show that neurine is intermediate in its physiological action between the curari and muscarine alkaloids.

V. H. V.

**Inhalation of Methane and Monochloromethane.** By J. REGNAULD and VILLEJEAN (*Compt. rend.*, **100**, 1024—1027).—When methane mixed with 3·5—5 times its volume of oxygen is inhaled by rabbits, guinea-pigs, and dogs, it exerts no physiological action whatever. When pure monochloromethane is inhaled, either mixed with air or with oxygen, it produces effects similar to those produced by chloroform; but the quantity of monochloromethane required to produce insensibility, in the case of dogs, is about double the quantity of chloroform required to produce the same effect. The complete return to normal physiological conditions requires an extremely short time, and this fact shows that monochloromethane is eliminated much more easily than any of the other chlorine-derivatives of methane.

C. H. B.

**Inhalation of Dichloromethane and Tetrachloromethane.** By J. REGNAULD and VILLEJEAN (*Compt. rend.*, **100**, 1146—1148).—Methane, when mixed with air or oxygen in suitable proportions is entirely without anæsthetic properties, even under pressure, but the substitution of chlorine for hydrogen produces compounds with anæsthetic properties. Of the four chlorine-derivatives of methane, those of the chloroform type,  $\text{CH}_3\text{Cl}$  and  $\text{CHCl}_3$ , are comparatively inoffensive, but the other two,  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$ , are extremely dangerous, producing symptoms very different from those produced by chloroform, and exerting a powerful poisonous action.

C. H. B.

**Formation of Alkaloids in Diseases.** By VILLIERS (*Compt. rend.*, **100**, 1078—1079).—The organs of two children who had died from broncho-pneumonia following upon measles, when treated by Stas's process, yielded a volatile liquid alkaloid with a sharp smell which excites sneezing, but no decided taste. It has no action on litmus, is easily soluble in ether, which removes it from its aqueous solutions, and is liberated by alkaline bicarbonates. It yields white or yellowish-white amorphous precipitates with mercurio-potassium iodide, iodine solution, bromine-water, mercuric chloride, and gold chloride, but no precipitates with platinic chloride, potassium dichromate, tannin or picric acid. The reaction with bromine-water is very delicate. The alkaloid is coloured reddish-brown by sulphuric acid, and slowly reduces potassium ferricyanide. It forms a hydrochloride, which crystallises readily in opaque white non-deliquescent prisms. This alkaloid is found in the lungs, liver, and kidneys. It differs considerably in its properties from the alkaloid already isolated from the organs of cholera patients (*Compt. rend.*, **100**, 91), but seems to be identical with an alkaloid which the author has obtained from the organs of a child who died from diphtheria, but was also affected with broncho-pneumonia. In both this and the first cases, the liver showed fatty degeneration.

C. H. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Diastase.** By E. BOURQUELOT (*J. Pharm.* [5], 11, 367—372).

—Diastase is widely distributed in nature, both in animals and plants. Most physiologists admit that malt diastase and that of human saliva determine the saccharification of starch, of glycogen, and of certain dextrins; but some maintain that these compounds possess other properties. The author, however, shows that the inversion of cane-sugar ascribed to the action of saliva diastase is really due to the invertin secreted by microphytes present in the saliva; the same action caused by malt diastase is due to invertin secreted by fungoid growths which can be found on the malt grains. The author maintains that all the diastases considered are identical. J. T.

**Evolution of Carbonic Anhydride and Absorption of Oxygen by Leaves in the Dark.** By P. P. DEHÉRAIN and L. MAQUENNE (*Compt. rend.*, 100, 1234—1238).—Leaves of *Euonymus japonica* were introduced into a glass tube which could be closed hermetically, and which was then rendered vacuous. A quantity of pure air was then allowed to enter the tube, which was kept at a constant temperature in the dark for some hours. At the close of the experiment, the gas was pumped out of the tube and analysed. The volume of nitrogen was always the same as that in the original air, but the ratio of the carbonic anhydride given off to oxygen absorbed  $\frac{\text{CO}_2}{\text{O}}$  was always greater than 1, whereas Bonnier and Mangin

obtained ratios equal to or less than 1. The authors find that if the gas is pumped out of the tube in successive portions, the last portions always contained a greater proportion of carbonic anhydride, and it would seem possible, therefore, that Bonnier and Mangin left some of the carbonic anhydride still in the leaves. The fact that the ratio  $\frac{\text{CO}_2}{\text{O}}$  is greater than 1 indicates that the respiration of leaves in the

dark is not accompanied by a simple conversion of oxygen into carbonic anhydride, but that internal combustion similar to fermentation also take place.

Schloesing points out that one of the great difficulties is to account for the fact that the hydrogen in an entire plant is always more than that required to form water with the oxygen present. C. H. B.

**Theory of the Circulation of the Sap in Plants.** By E. GODLEWSKI (*Ann. Agronom.*, 11, 165—191).

**Chaulmoogra Seeds (*Gynocardia Odorata*).** By E. HECKEL and F. SCHLAGDENHAUFFEN (*J. Pharm.* [5], 11, 359).

**Analysis of Tobacco.** (*Bied. Centr.*, 1885, 284—285).—The object of the various analyses, which are given in full detail, was



to determine if possible the influence of the ash on the combustibility of the leaf; but no definite results have been arrived at, further than that the leaf burns well if it be rich in organic potassium salts, in sulphates, and cellulose; but sugar, mucilage, and albuminoids are a hindrance to combustibility, as are also such salts as fuse at the temperature at which tobacco burns, namely, chlorides and phosphates of the alkalis. Sugar, albuminoids, and probably organic acids, are reduced in quantity by fermentation, consequently manufactured tobacco burns with greater readiness.

E. W. P.

**Composition of Horse Chestnuts.** By J. HANAMANN (*Bied. Centr.*, 1885, 263—265).—The following analysis represents the maximum and minimum amounts of the constituents of horse chestnuts, obtained from various localities:—

	Water.	Albuminoids.	Fat.	Matter capable of conversion into sugar.	Ash.
Maximum..	10·27	8·75	7·07	76·39	2·51
Minimum..	7·08	6·56	5·08	72·94	2·17
Nutritive value, 1 : 7.					

The percentage of the ash constituents is also given. E. W. P.

**Absorption of Water by Beetroots.** By H. BRIEM (*Bied. Centr.*, 1885, 265—267).—When kept, beets absorb water, although before hoddling they lose water; this increase will probably account for the apparent loss of sugar by keeping.

E. W. P.

**Experimental Culture of Wheat at Grignon in 1884.** By P. P. DEHÉRAIN (*Ann. Agronom.*, 11, 145—165).—The results of the three series of experimental plots carrying respectively wheat after sugar-beet, wheat after forage maize, and wheat after flax, with various manures, are detailed in this paper, and an attempt is made to compare the cultures from an economical standpoint. The price of wheat having fallen to 20 francs per quintal, a great many farmers have declared the impossibility of growing it profitably at that price, and the Government has imposed a duty of 3 francs per quintal on imported wheat. The unmanured plots at Grignon furnished in 1884 an average of 25 hectolitres of grain per hectare, whereas the average yield of the whole country is estimated in good years at 15 hectolitres, and when to obtain this 15 hectolitres perhaps 100 francs have been spent in manure, there is obviously little or no margin for profit. Much higher yields than 25 hectolitres were obtained at Grignon on the plots which had received suitable manures both for the wheat and for the preceding crop, and this year, as in former years, the wheat and preceding green maize, considered together, yielded a far better return than wheat preceded by either sugar-beet or flax. A heavy dressing of farmyard manure for the maize, with or without nitrate of soda, followed by a similar but smaller dressing for the wheat, produced the largest crops, but a better net return was obtained by

growing the wheat without manure. As regards flax and the succeeding wheat crop, if the flax be supposed to pay its own expense of manuring and cultivation, the wheat after it shows a rather better net return than the sugar-beet and wheat taken together. Chloride of potassium, in conjunction with nitrate of soda, produced a striking result on wheat after flax, but the good effect of potassium salts at Grignon is exceptional rather than general. The author recommends the general use of nitrate of soda for wheat crops on poor soil, and, when no farmyard manure has been applied, 200 kilos. per hectare of nitrate of soda mixed with 100—200 kilos. chloride of potassium is suggested as a good dressing. J. M. H. M.

**Composition of Alpine and Valley Hay.** By W. EUGLING (*Bied. Centr.*, 1885, 250—252).—Analyses of hay from various localities are given. The general deductions to be drawn are that although the height at which it grows and the character of the soil has but little influence on the principal constituents of the hay, yet hay growing at a height of 1200—1400 metres is somewhat low in fibre and ash; there appears also to be a slight increase of albuminoids in the hay grown in high localities. E. W. P.

**Nutritive Value of Hay grown on Marsh Lands.** By PETERSEN (*Bied. Centr.*, 1885, 252—253).—Analyses of two samples of hay, the one grown on alluvium, and the other on land lying on “Knick” and “Wühlerde” are given. The second sample is richer in ash and protein, but poorer in fibre, than the first; the nutritive value of the first is 1 : 8·3, of the second 1 : 50. E. W. P.

**Influence of Malt Coombs, and the Non-Albuminoids contained in them on the Yield of Milk.** By M. SCHRODT and H. HANSEN (*Bied. Centr.*, 1885, 246—248). The cows were fed under the usual conditions with malt coombs, replacing in part clover, hay, and bran. This fodder, which contains much nitrogen as amides, was found to reduce the total yield to a small extent, but the diminution in the percentage of fat and solids was very slight. E. W. P.

**Experiments with Nitrogenous Peaty Soils.** By W. EUGLING (*Bied. Centr.*, 1885, 228—229).—Peaty soil was mixed with precipitated chalk, and small quantities of calcium phosphate and ammonium sulphate were added; in this soil, soja beans were sown, and they grew normally. At the end of the experiment, the soil which originally contained 15,330 grams dry matter, had lost 555 grams dry matter, the crops at the same time weighing 625 grams. As regards the nitrogen, the soil appears to have been enriched by 11·9 per cent. of the total original nitrogen. E. W. P.

**Action of Sea Mud on Peaty and Sandy Soils.** By M. FLEISCHER and others (*Bied. Centr.*, 1885, 233—245). A detailed account of the amelioration of moorland and sandy soils, and of the crops grown on them. E. W. P.

**Complementary Manures.** By DE GASPARIN (*Compt. rend.*, 100, 932—934).—The author points out the necessity of adapting the manure not only to the crop which is to be grown, but also to the actual composition of the soil, with special regard to the assimilable or non-assimilable condition of the various constituents of the soil.

C. H. B.

**Nitrogen in Leather Waste.** By R. DANGUY (*Bied. Centr.*, 1885, 278).—The percentages of nitrogen in various leathers are given; they vary from 6.45 (salted American bullock hide) to 3.42 (black Levant goat, cured in England).

E. W. P.

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## Analytical Chemistry.

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**New Dropping Flask.** By F. V. POOL (*Chem. News*, 51, 219).—In place of burettes, the author recommends the use of a light and flat-bottomed flask, which, at one side, near the bottom, has a thin tube, exactly similar to that in the Gay-Lussac burette, passing up to just above the body of the flask. The neck has a small hole in the side, and the mouth is closed by a stopper, through which passes a short thistle-head tube, with a piece of sheet india rubber stretched and tied over the top. When in use, the thumb covers the hole in the side of the neck, and the index finger rests on the membrane, the manipulation is obvious. The flask and contents are weighed before and after the titration.  
D. A. L.

**Determination of Nitrogen by the Copper Oxide Method and the Comparison of this and the Ruffle Method.** By C. W. DABNEY and B. VON HERFF (*Chem. News*, 51, 244—247).—Comparative experiments with a large and very varied set of nitrogenous substances, show that the Ruffle method and the copper oxide method give equally good results. The results are apt to be low in the first case, and high in the second.  
D. A. L.

**Kjeldahl's Method of Nitrogen Estimation.** By C. ARNOLD (*Arch. Pharm.* [3], 23, 177—185).—The author insists on the simplicity and trustworthiness of this method, which has been already described (*Abstr.*, 1884, 364). The results obtained with various organic substances agree closely with those obtained by Dumas and Zulkowski's method.  
J. K. C.

**Estimation of Nitric Acid by Means of Diphenylamine and Potassium-stannous Sulphate.** By C. W. MOULTON (*Chem. News*, 51, 207).—This method (this vol., p. 595) does not answer with very dilute solutions of nitrates; for owing to the slowness of the reaction, the volume of the liquid tested, and the time occupied, become more important factors than the quantity of nitrate present.  
D. A. L.

**Estimation of Phosphoric Acid in Commercial Products.** By H. JOULIE (*Ann. Agronom.*, **11**, 97—129).—The author gives a critical description of the estimation of the total phosphoric acid in manures, &c., the method being based on the precipitation of the phosphoric acid as ammonium magnesium phosphate, the precipitate is then either dissolved and titrated with uranium acetate, or weighed as magnesium pyrophosphate, or dissolved and precipitated with ammonium molybdate. The manipulation and precautions necessary at all stages, together with the incidental errors, are described in full detail.

A. J. G.

**Determination of Sulphur in Proteïds.** By O. HAMMARSTEN (*Zeit. physiol. Chem.*, **9**, 273—309).—See p. 914.

**New Indicators for the Estimation of Hydroxides in Presence of Carbonates.** By R. ENGEL and J. VILLE (*Cmpt. rend.*, **100**, 1073—1074).—A solution of sulphindigotic acid obtained by neutralising a solution of indigo in fuming sulphuric acid with calcium carbonate, diluting with 10 vols. of water, and filtering, can be used as an indicator in alkalimetry. It is not affected by alkaline carbonates, but is turned yellow by alkaline hydroxides, and therefore can be used for the estimation of the latter in presence of the former. The end reaction is not perfectly sharp, the blue colour being preceded by green, but the addition of acid is continued until a fresh drop produces no visible change at the point where it falls into the liquid.

Porrier's soluble blue C4B dissolved in 500 times its weight of water is a still more sensitive reagent, and can be used for the same purpose. It remains blue in presence of alkaline carbonates, but is turned red by alkaline hydroxides. When sulphuric acid is added to a mixed solution of alkaline hydroxide and carbonate containing a small quantity of this indicator, the distinctly blue colour which marks the end of the reaction is preceded by a violet shade.

C. H. B.

**Phenolphthaleïn as an Indicator.** By E. LÉGER (*J. Pharm.* [5], **11**, 425—428).—The author has observed that certain organic alkaloids have no action on phenolphthaleïn; thus the presence of morphine, quinine, &c., does not interfere with the titration of sulphuric acid, the same holds true with regard to hydrochloric and nitric acids. Cicutine and codeine are the only organic bases as yet found to affect this indicator. The author details experiments and concludes that—(1.) It is possible to estimate an acid volumetrically as easily when combined with certain alkaloids as when in the free state. (2.) This estimation may serve within certain limits to indicate the purity of a salt of the alkaloid.

J. T.

**Lakmoïd and Carminic Acid as Reagents for Alkalis.** By H. N. DRAPER (*Chem. News*, **51**, 206—207).—Lakmoïd (Traube and Hock, this vol., p. 148) and carminic acid form extremely delicate test reagents for alkalis and are both more delicate than litmus. The former distinctly indicates about five parts of calcium carbonate in a million of water, the reaction being rendered more decided by dilution with distilled water, owing to the withdrawal of carbonic anhydride.

Carminic acid is, perhaps, the best, as its change in colour is more decided, and it is less affected by carbonic anhydride. D. A. L.

**Separation of Zinc from the Metals of the same Group.** By W. HAMPE (*Chem. News*, 51, 230).—To separate zinc from iron, nickel, cobalt, manganese, and aluminium, the metals are converted into formates, and the hot solution containing free formic acid is treated with hydrogen sulphide, which precipitates zinc sulphide only. If, however, an insufficient quantity of formic acid is present, or if the other metals are present in large excess, then the zinc sulphide may be contaminated, and should be dissolved, converted into formate and reprecipitated. D. A. L.

**Titration of Iron Ores.** By W. HEMPEL (*Ber.*, 18, 1130—1132).—Iron ores are conveniently and quickly assayed by roasting them for about an hour in a muffle with 20 parts of calcium carbonate and 4 parts of sodium carbonate (free from iron); the iron is thus obtained in the form of ferric oxide, the formation of ferric silicate is avoided, and any organic matter present is removed, the roasted mass is very readily soluble in hydrochloric acid, and after boiling for 30 minutes to get rid of any free chlorine which may be formed, the solution is diluted and the iron titrated with stannous chloride. Magnesium carbonate may be used instead of calcium carbonate.

A. P.

**Quantitative Analysis by Electrolysis.** By A. CLASSEN and R. LUDWIG (*Ber.*, 18, 1104—1114).—A continuation of the author's previous work on this subject (this vol., p. 190).

**Separation of Arsenic, Antimony, and Tin.**—The metals are first converted into chlorides, ferric chloride is added and the arsenic is distilled off in a current of hydrogen chloride, the distillate being conveyed into water; the solution is then diluted with water, the air is displaced by carbonic anhydride, and the arsenic precipitated with hydrogen sulphide. The arsenious sulphide is dissolved in excess of ammonia, the sulphur oxidised into sulphuric acid by treatment with excess of hydrogen peroxide, and the arsenic calculated from the sulphuric acid formed. The strongly acid solution remaining after the distillation of the arsenic is diluted with water. The antimony and tin are precipitated by hydrogen sulphide, the precipitate is washed free from acid and dissolved in about 60 c.c. of pure sodium sulphide, about 1 gram of sodium hydroxide is then added in concentrated aqueous solution, the solution is placed in a perfectly smooth platinum dish and electrolysed, the current being passed for about 12 hours, when all the antimony is obtained as a thin shining layer firmly attached to the dish. The sodium sulphide containing the tin in solution is converted into ammoniac sulphide by ammonium sulphate, and the solution is electrolysed by a current yielding from 9 to 10 c.c. of electrolytic gas per minute; the precipitation is complete in 4—5 hours. If the antimony and arsenic are in solution in an alkaline polysulphide, it is necessary to convert the latter into the monosulphide by warming with an ammoniacal solution of hydrogen peroxide until the solution becomes colourless or a slight precipitate is formed, the solution is

evaporated almost to dryness, sodium monosulphide and hydroxide added, and the process proceeded with as above. A. P.

**Estimation of Cyanogen in Gaseous Mixtures.** By G. JACQUEMIN (*Compt. rend.*, 100, 1006—1007).—In mixtures of cyanogen, carbonic anhydride, carbonic oxide, oxygen, and nitrogen, the cyanogen can be absorbed by manganese peroxide, mercuric oxide, red lead, or lead peroxide in presence of water. Acetic acid of 95 per cent. will also absorb 80 times its volume of cyanogen, but the best absorbent is aniline, which combines with the cyanogen to form cyananiline, but has no action on carbonic anhydride, carbonic oxide, or air.

C. H. B.

**Detection of Chloral Hydrate.** By VITALI and TORNANI (*Arch. Pharm.* [3], 23, 234—235).—The method admits of the detection of chloral in the presence of chloroform, and conversely. The suspected matter is mixed with water when necessary, strongly acidified with tartaric acid, and distilled to dryness in a gentle current of carbonic anhydride, the receiver being well cooled by means of ice. Experiment shows that both chloroform and chloral pass over completely. The distillate is again acidified with tartaric acid, and a gentle current of hydrogen is passed through in a special apparatus. All the chloroform is thus carried off whilst only traces of chloral volatilise; the latter is arrested by an interposed column of sulphuric acid. The escaping steam of hydrogen is burnt at a platinum jet, and on bringing a piece of brass gauze into the flame a beautiful blue copper chloride flame is produced if chloroform is present in the gas, and the products of combustion when drawn through an ammonia solution give an azure-blue colour. On acidifying this solution with nitric acid, the chlorine can be precipitated, and the amount of chloroform then deduced. When all the chloroform is expelled, the distillate is treated with excess of potash, and the gas is again passed through. All the chloroform now obtained can only be from the decomposition of the chloral hydrate. It may be added that the qualitative detection of chloroform in the hydrogen current can also be obtained by passing the gas into a solution of thymol in potash, which gives an intense violet colour with chloroform.

J. T.

**Determination of Free Sulphuric Acid in Vinegar.** By B. KOHNSTEIN (*Dingl. polyt. J.*, 256, 128—130).—100 c.c. of vinegar are completely neutralised with freshly ignited pure magnesium oxide. 25 to 30 c.c. of the filtrate are evaporated to dryness in a platinum dish, and ignited at a moderate temperature. The magnesium acetate is converted into magnesium carbonate, whilst the sulphate which remains unaltered is extracted with water charged with carbonic anhydride, and after removing the lime in the filtrate the magnesium is estimated as pyrophosphate, and from it the quantity of free sulphuric acid contained in the vinegar is calculated.

D. B.

**Estimation of Resin in Soap.** By G. HEINER (*J. Pharm.* [5], 11, 434—435).—The author obtained discordant results in attempting to estimate resin in (black) soaps by Hager and Jungst's method. He

recommends the following method :—A portion of the soap is decomposed by means of sulphuric acid, and the resinous and fatty acids separated are weighed. A second portion is dissolved in water and precipitated by a solution of common salt. The resin remains as an emulsion with the glycerol; the separated soap is washed with salt solution, dissolved in distilled water, decomposed by means of sulphuric acid, and the fatty acids weighed as in the first portion. The difference gives the amount of resin. A soap prepared with 20 per cent. of resin gave 18·19 and 18·54 per cent. on analysis. J. T.

**Testing Oil of Roses.** By F. A. FLÜCKIGER (*Arch. Pharm.* [3], 23, 185—188).—Adverting to Helm's statement that in four samples of Turkish oil of roses he had found no stearopten, the author remarks that the oil from that source is invariably adulterated. Working on a sample of oil made in the laboratory from roses grown in the neighbourhood of Leipzig, the author found 28·8 per cent. of stearopten.

J. K. C.

**Reagent for Aromatic Diamines.** By O. HINSBERG (*Ber.*, 18, 1228).—The author has found the following test useful for detecting traces of orthophenylenediamine in metaparatoluylenediamine. A drop of a hot solution of phenanthraquinone in glacial acetic acid is added to the alcoholic solution of the substance and the mixture boiled; if the orthodiamine is present, a voluminous precipitate of yellow needles is obtained; these give a deep red coloration when moistened with hydrochloric acid.

A. J. G.

**Indigo Testing.** By H. M. RAU (*Chem. News*, 51, 207—208).—The following modification of Fritsche's method is recommended:—About 2 grams of the finely powdered sample are introduced into a flask fitted with a doubly bored rubber stopper, through which pass a tube provided with a stopcock, and a syphon-tube reaching nearly to the bottom of the flask and terminating in an inverted funnel, which is filled with glass-wool; the whole arrangement is weighed, and about 20 c.c. of a 40 per cent. caustic soda solution, 60 c.c. water, and about 120 c.c. of 70 per cent. alcohol are added, the whole apparatus is again weighed. The syphon is now closed, the flask heated on a water-bath, relieving pressure from time to time, until solution is complete; after an hour the clear liquid is poured off through the syphon, and in order to ascertain the quantity the flask is quickly weighed again. The indigotin and indirubin are precipitated from the liquid in crystalline flakes by means of a current of carbonic anhydride; the precipitate is filtered, washed, dried, and weighed. From the weight so obtained, the amount of indigo present is calculated.

D. A. L.

**Estimation of Tannins by Lowenthal's Method.** By R. ULBRICHT (*Ber.* 18, 1116—1119).

**Estimation of Tannin.** By F. BECKER (*Chem. News*, 51, 229).—Into 50 c.c. of a solution containing 5 grams of methyl-violet per litre, mixed with 450 c.c. of water and heated at 50°, a solution of



pure tannin containing 10 grams per litre is run until all the colouring matter is precipitated and the filtrate from it is colourless, the quantity of tannin used being noted. A solution of similar strength of the tannin to be examined is treated in a similar manner, and its relative value calculated from the figures obtained. Other astringent dye-materials may be tested by this method; sumach, for example, being made up to 20 to 40 grams per litre. D. A. L.

**Determination of the Free Acids contained in Tannin Liquor.** By B. KOHNSTEIN and F. SIMAND (*Dingl. polyt. J.*, **256**, 38—42).—On agitating tannin liquor with an excess of magnesium oxide, the tannin is completely precipitated as magnesium tannate, whilst the amount of magnesium remaining in solution is equivalent to the total free acids.

The volatile organic acids (acetic acid, butyric acid, &c.) are determined by distilling 100 c.c. of the liquor to 30 c.c. The residue is made up with water to the original volume, redistilled, and this is repeated until the distillate measures 300 c.c., when it is titrated and calculated into acetic acid.

**Determination of the Non-volatile Organic Acids (Lactic Acid).**—80 c.c. of the liquor are treated with 3–4 grams of freshly ignited magnesium oxide, filtered, 10–30 c.c. of the filtrate are evaporated and ignited gently, washed with carbonic acid water, and the magnesium carbonate in the residue estimated and calculated into the equivalent of acetic acid; deducting therefrom the volatile acid, the percentage of acetic acid corresponding to non-volatile organic acids is obtained. The latter is then calculated into lactic acid.

**Determination of the Mineral Acids (Sulphuric Acid).**—In the filtrate from the magnesium carbonate precipitate, which contains magnesium sulphate, the magnesium is determined and calculated as sulphuric acid. D. B.

**Quantitative Determination of Asparagine and Glutamine.** By E. SCHULZE (*J. pr. Chem.* [2], **31**, 233—246).—In employing Sachsse's method for estimating asparagine in vegetable juices, &c., namely the estimation of the nitrogen set free by sodium hypobromite solution before and after boiling with dilute hydrochloric acid, a larger amount of nitrogen is liberated than is required by theory. This is found to be due to the further action of the hypobromite in presence of ammoniacal salts, or of carbamide; and it is therefore found better to estimate the ammonia formed by the decomposition of asparagine by Schlösing's method of distillation with magnesia. The existence of other nitrogenous bodies in vegetable juices and their influence on the estimation of asparagine is discussed. H. B.

**Estimation of Quinine in Mixtures of Quinine-Alkaloids.**—By Y. SHIMOYAMA (*Arch. Pharm.* [3], **23**, 209—229).—The method described is founded on the relative solubilities of the oxalates of the quinine alkaloids:—Quinine oxalate dissolves in 1446 parts of water at 18°; cinchonidine oxalate in 228 parts at 15°; quinidine oxalate in 151 parts at 15°, and cinchonine oxalate in 104 parts

at 10°. The precipitation is effected by adding sodium oxalate to a dilute neutral solution of the alkaloids, and correction must be made for the amount of quinine oxalate remaining in solution. J. T.

**Determination of Casein in Cow's Milk.** By J. FRENZEL and T. WEYL (*Zeit. physiol. Chem.*, 9, 246—252).—The method proposed in this paper is that of precipitation by dilute sulphuric acid, after previously diluting the milk with 3 vols. water. The results obtained by this method are compared with those of Hoppe-Seyler's, which consists in acidification with acetic acid after previously diluting the milk to 20 vols., and completing the precipitation by passing a stream of CO<sub>2</sub>. The effect of varying the conditions of precipitation was also investigated.

The results differ but slightly from those obtained by Hoppe-Seyler's method, over which the authors' has the advantage of being more expeditious. C. F. C.

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## Technical Chemistry.

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**Behaviour of the Haloïd Salts of Silver in the Solar Spectrum: Orthochromatic Photography.** By J. M. EDER (*Ber.*, 18, 1265—1267).—A reply to Vogel (this vol., p. 846).

**Purification of Drinking Water by Alum.** By P. T. AUSTEN and F. A. WILBER (*Chem. News*, 51, 241—244).—The authors strongly advocate the use of alum for the purification of water, alleging that it not only clarifies but also removes disease germs and ptomaines.

By adding 2 grams of alum to 60 litres of a rather turbid drinking water, a precipitate settled, and perfectly clear water was obtained after 48 hours. The dried precipitate contained per cent. C 16·50, H 2·02, N 0·77, ash 59·28, the latter consisting of small amounts of silica and alumina, large amounts of iron oxide, and considerable quantities of phosphoric acid. The clear water contained the merest trace of aluminium, and a further addition of alum caused no precipitation in it.

D. A. L.

**Reducing Action of Coke on Nitric Acid.** By G. LUNGE (*Dingl. polyt. J.*, 256, 96).—To confirm the observation that the so-called "nitrous vitriol" of the Gay-Lussac towers only contains nitrous acid, if the gases on entering the tower contain considerable quantities of nitrogen tetroxide, the author tested the action of coke on nitric acid, and found that the nitric acid dissolved in sulphuric acid in contact with coke is reduced to nitrogen trioxide slowly at the ordinary temperature, but quickly and practically completely at a slightly elevated temperature, such as usually exists in the Gay-Lussac tower. Whether the reduction is effected directly by the

carbon or by sulphurous anhydride produced by the action of the coke on sulphuric acid, the experiment does not show. D. B.

**Obtaining Sulphur from Hydrogen Sulphide.** (*Dingl. polyt. J.*, 256, 143.)—The *Oesterreichische Sodafabrik in Hruschau* has patented a process for recovering the sulphur from sulphuretted hydrogen, which consists in passing the latter through heated sulphates of the alkalis or alkaline earths, the result being the combination of the oxygen contained in these salts with the hydrogen of the gas, and the formation of free sulphur, the residue containing the respective metallic sulphides. By blowing atmospheric oxygen into the latter, and continuing the heating process, the metallic sulphide is oxidised into the sulphate, which is then used for another operation. D. B.

**Manufacture of Strontium Hydroxide and Sodium Hydrosulphide.** By C. F. CLAUS (*J. Pharm.* [5], 11, 434).—The process is based on the decomposition of strontium monosulphide into hydroxide and hydrosulphide under the influence of water; the hydroxide crystallises out. The mother-liquor containing hydrosulphide may be treated with sodium sulphate, separating the strontium sulphate precipitated, and evaporating the solution to obtain sodium hydrosulphide (to obtain a colourless product, iron vessels must be avoided): or the liquid is mixed with magnesium sulphate, and heated to eliminate all the hydrogen sulphide; the mixture of strontium sulphate and magnesium hydroxide is then exposed to a current of carbonic anhydride, by which strontium carbonate and magnesium sulphate are produced. J. T.

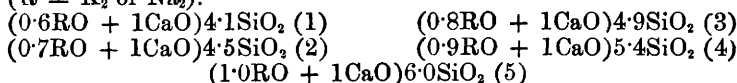
**Calculation of Glass Batches.** By E. TSCHESCHNER (*Dingl. polyt. J.*, 256, 75—84).—Although the chemical constitution and the composition of glass has been the subject of research during the last ten years, the results do not appear to have led to a solution of the question relating to the formation of glass batches. It is a generally-accepted fact that the various constituents of glass are present in a ratio corresponding to a double union of a trisilicate of an alkali and an alkaline earth; but the proportion between these compounds, although subject to wide differences, still remains undetermined. The author has attempted to solve this problem, and establish a relationship between the proportion of alkalis and earths and the stages of silicification. If in the analysis of glass the amount of alkalis, earths, and silicic acid (expressed in equivalent quantities) be summarised, the first designated as AO, the second as EO, and the third as SiO<sub>2</sub>, the formula  $x\text{AO} + y\text{EO} + z\text{SiO}_2$ , is obtained for the composition of the glass; the coefficients  $x$ ,  $y$ ,  $z$  being numbers which are subject to variations within certain limits. For the normal composition these coefficients would assume the values  $x = y = 1$ ,  $z = 6 = 3(x + y)$ . The formula  $z = 3(x + y)$  which determines the quantity of silicic acid to be added to a glass containing a certain amount of alkalis and earths only holds good if  $x = y$ . For instance, applied to the glasses analysed by Weber (*ibid.*, 232, 349), the following numbers are obtained:—

No. of analysis.	$x$ .	$y$ .	$3(x + y)$ .	$z$ .	$3\left(\frac{x^2}{y} + y\right)$ .
32	0.60	1	4.80	4.0	4.1
33	0.60	1	4.80	4.2	4.1
34	0.88	1	5.64	5.3	4.8
35	0.90	1	5.70	5.3	5.4
36	0.90	1	5.70	5.2	5.4
37	0.60	1	4.80	4.4	4.1
38	0.60	1	4.80	3.8	4.1
39	2.00	1	9.00	12.5	15.0
40	1.50	1	7.50	9.6	9.75
42	1.50	1	7.50	8.8	9.75
43	0.85	1	5.55	5.2	5.20
47	0.33	1	3.99	3.5	3.33

By comparing the calculated values of  $3(x + y)$  in column 4 with the values of  $z$  in column 5, which have been obtained by actual analysis, it will be seen that when the percentage of alkali is high, the values in column 4 are too low, and when low the values are too high. However, by increasing the  $x$  in the value  $3(x + y)$  in proportion to the quantity of alkali, and diminishing it in proportion to the lime present, the values contained in the last column are obtained. These agree more closely with the  $z$  values. The normal formula for the composition of glasses may therefore be expressed thus:—

$x\text{AO} + y\text{EO} + 3\left(\frac{x^2}{y} + y\right)\text{SiO}_2$ . For  $y = 1$  the value for  $x$  in the case of plate glass may range between 0.6 and 1.0, in the case of Bohemian glass between 1.5 and 2.0, and in the case of hollow glassware between 0.8 and 1.5. The author gives the following formulæ for the composition of plate glass according to the above data:—

(R =  $\text{K}_2$  or  $\text{Na}_2$ ).



According to formula (1), the percentage composition of the corresponding potash-lime and soda-lime glass may be expressed by the following numbers:—

Potash-lime glass.			Soda-lime glass.		
1a.			1b.		
$0.6 \times 47.1 =$	$28.26 =$	$15.7\text{K}_2\text{O}$	$0.6 \times 31 =$	$18.6 =$	$11.0\text{Na}_2\text{O}$
$1.0 \times 28.0 =$	$28.00 =$	$15.6\text{CaO}$	$1.0 \times 28 =$	$28.0 =$	$16.5\text{CaO}$
$4.1 \times 30.0 =$	$123.00 =$	$68.7\text{SiO}_2$	$4.1 \times 30 =$	$123.0 =$	$72.5\text{SiO}_2$
<hr/>			<hr/>		
$179.26 = 100.0$			$169.6 \quad 100.0$		

For the remaining formulæ we obtain—

Potash-lime glass.

2a.

$$\begin{array}{rcl} 0.7 \times 47.1 & = & 32.97 = 16.8\text{K}_2\text{O} \\ 1.0 \times 28.0 & = & 28.00 = 14.3\text{CaO} \\ 4.5 \times 30.0 & = & 135.00 = 68.9\text{SiO}_2 \\ \hline & & 195.97 \quad 100.0 \end{array}$$

3a.

$$\begin{array}{rcl} 0.8 \times 47.1 & = & 37.68 = 17.7\text{K}_2\text{O} \\ 1.0 \times 28.0 & = & 28.00 = 13.2\text{CaO} \\ 4.9 \times 30.0 & = & 147.00 = 69.1\text{SiO}_2 \\ \hline & & 212.68 \quad 100.0 \end{array}$$

4a.

$$\begin{array}{rcl} 0.9 \times 47.1 & = & 42.39 = 18.2\text{K}_2\text{O} \\ 1.0 \times 28.0 & = & 28.00 = 12.1\text{CaO} \\ 5.4 \times 30.0 & = & 162.00 = 69.7\text{SiO}_2 \\ \hline & & 232.39 \quad 100.0 \end{array}$$

5a.

$$\begin{array}{rcl} 1.0 \times 47.1 & = & 47.1 = 18.4\text{K}_2\text{O} \\ 1.0 \times 28.0 & = & 28.0 = 11.0\text{CaO} \\ 6.0 \times 30.0 & = & 180.0 = 70.6\text{SiO}_2 \\ \hline & & 255.1 \quad 100.0 \end{array}$$

Soda-lime glass.

2b.

$$\begin{array}{rcl} 0.7 \times 31 & = & 21.7 = 11.7\text{Na}_2\text{O} \\ 1.0 \times 28 & = & 28.0 = 15.2\text{CaO} \\ 4.5 \times 30 & = & 135.0 = 73.1\text{SiO}_2 \\ \hline & & 184.7 \quad 100.0 \end{array}$$

3b.

$$\begin{array}{rcl} 0.8 \times 31 & = & 24.8 = 12.4\text{Na}_2\text{O} \\ 1.0 \times 28 & = & 28.0 = 14.0\text{CaO} \\ 4.9 \times 30 & = & 147.0 = 73.6\text{SiO}_2 \\ \hline & & 199.8 \quad 100.0 \end{array}$$

4b.

$$\begin{array}{rcl} 0.8 \times 31 & = & 27.9 = 12.8\text{Na}_2\text{O} \\ 1.0 \times 28 & = & 28.0 = 12.8\text{CaO} \\ 5.4 \times 30 & = & 162.0 = 74.4\text{SiO}_2 \\ \hline & & 217.9 \quad 100.0 \end{array}$$

5b.

$$\begin{array}{rcl} 1.0 \times 31 & = & 31.0 = 13.0\text{Na}_2\text{O} \\ 1.0 \times 28 & = & 28.0 = 11.7\text{CaO} \\ 6.0 \times 30 & = & 180.0 = 75.3\text{SiO}_2 \\ \hline & & 239.0 \quad 100.0 \end{array}$$

To manufacture white plate glass according to 4b from Nievelstein sand containing 99 per cent.  $\text{SiO}_2$ , ammonia-soda containing 98 per cent.  $\text{Na}_2\text{CO}_3 = 57.3\text{Na}_2\text{O}$ , or calcined Glauber salt with 96 per cent.  $\text{Na}_2\text{SO}_4 = 42$  per cent.  $\text{Na}_2\text{O}$ , and ground calcspar containing 97 per cent.  $\text{CaCO}_3 = 54.3$  per cent.  $\text{CaO}$ , the following quantities are required :—

$$\begin{array}{l} (12.8 \times 100) : 57.3 = 22.3 \text{ kilos. soda, or } 30 \text{ kilos.} \\ (12.8 \times 100) : 54.3 = 23.6 \text{ ,, calcspar, or } 32 \text{ kilos.} \\ (74.4 \times 100) : 99.0 = 74.2 \text{ ,, sand, or } 100 \text{ kilos.} \end{array}$$

If sulphate is used, we obtain—

$$\begin{array}{l} (12.8 \times 100) : 42.0 = 30.5 \text{ kilos. sulphate.} \\ (12.8 \times 100) : 54.3 = 23.6 \text{ ,, calcspar.} \\ (74.4 \times 100) : 99.0 = 74.2 \text{ ,, sand.} \end{array}$$

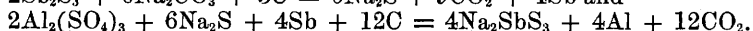
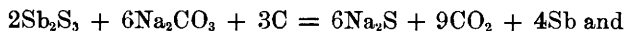
or calculated on 100 parts of sand—

Sand .....	100.00
Sulphate .....	41.00
Calcspar .....	42.00
Coal for reduction of sulphate.....	2.75

D. B.

**Preparation of Magnesium.** By GRAETZEL (*Arch. Pharm.* [3], 23, 233).—The author has patented a method for producing magnesium by electrolysis, which is said to reduce the price from 250—300 marks per kilo. to 80 marks. J. T.

**Novelties in Metallurgy.** (*Dingl. polyt. J.*, 256, 226—233.)—For the production of aluminium, Lauterborn proposes to fill a furnace with coke, blow air into the same, and introduce a mixture of aluminium sulphate, sodium carbonate, and antimony sulphide. The following reactions are said to occur:—



In order to obtain ammonia in the process of recovering tin or zinc from old metal, Reinecken recommends the employment of sodium nitrate as an oxidising agent; this, in acting on tin, loses oxygen and splits up into soda and ammonia, thus:—



According to Manhès, copper ores containing gold and silver are ground, mixed with 1—3 per cent. ammonium chloride, and heated in a muffle furnace at a moderate temperature until all fumes of ammonia have been expelled. The gold and silver are converted into chlorides, whilst the other constituents remain in combination with sulphur. The chlorides are dissolved by treatment with sodium thiosulphate.

E. Probert proposes to fuse auriferous or argentiferous arsenical or sulphur ores with litharge or lead, in crucibles lined with dolomite.

Howard recommends the decomposition of copper ores by a mixture of hydrogen potassium sulphate, hydrofluoric acid, sodium nitrate, sulphuric acid, and water.

Symons (*Berg- und Hütt.-Zeitung*, 1885, 58) discusses the production of copper from poor ores found at Maidanpec in Servia; and Brand (*ibid.*, 1885, 105) makes some important contributions to the knowledge of the changes occurring in the production of steel by smelting in acid and basic crucibles. D. B.

**Working-up Basic Slag.** By H. SCHÜCHTERMANN (*Dingl. polyt. J.*, 256, 190).—The slag is broken up into small pieces, freed from particles of metallic iron, mixed with a solution of calcium chloride, dried and heated in the presence of steam. The acids in combination with metallic oxides, such as sulphuric, silicic, and phosphoric acids, are said to be separated by this treatment, and combine with the lime, from which the phosphates are extracted in the usual manner. D. B.

**Application of Electricity in Chemical Industry.** (*Dingl. polyt. J.*, 255, 526—534.)—For the production of galvanic deposits on iron, Wagner and Jobst propose to galvanise cast iron in the usual manner, dip the material into a solution containing 3 grams of mercuric nitrate, 8 litres of water, and 7 litres of sulphuric acid, wash the mass thoroughly with water, and suspend it in a bronze-copper or similar bath.

Wagener and Netto recommend a process for producing metallic deposits on large plates, or similar materials, without immersion, which consists in connecting the articles with the negative pole, and causing the other electrode, which is covered with flannel kept saturated by the bath, to pass over the surface of the materials to be treated.

According to Froelich, the electric current is well adapted to the purification of metals, more especially for the removal of the last traces of foreign ingredients, which, in most cases, it is difficult to effect by other means. The first and most extensive plant for refining copper by electrolysis was erected in the autumn of 1878 at the Oker Smelting Works, situated in the Harz mountains. A number of Siemens machines are at the present time in operation, each depositing from 250 to 300 kilos. of copper daily, the consumption being equal to from 7 to 8 e. The copper to be treated passes through a preliminary refining process, and although it contains only 0·3 to 0·5 per cent. of impurities, the electrolytic process is said to be a financial success, owing to the increased value of the resulting copper. The great advantage of this process over the ordinary refining processes is that by its use the rare metals, more especially the silver, remain undissolved, and may be readily separated from the sludge which accumulates at the bottom of the bath. The only disadvantage of the electrolytic treatment is the behaviour of arsenic and antimony. These metals, if present, are dissolved in the bath, and pass into the deposited copper as soon as the bath is charged with a certain proportion of these metals. To overcome the difficulty, it is necessary to purify the bath, or replace the same more frequently.

The purification of silver by electrolysis is conducted at Moebius, in Mexico, where two Siemens machines are at work. It is not, however, possible to refine the silver to the same degree of purity as that which characterises electrolytically precipitated copper. Experiments have been made to convert hard lead into refined lead (soft) by electrolytic means, but without success, as the difference between the price of hard and soft lead is not sufficient to admit of the additional treatment.

A further application of electrolysis to metallurgical operations is the production of tin from old tin plate. Akerblom recommends the following method for the electrolytic determination of copper in arsenical ores, slags, &c. From 1—5 grams of ore is placed in a porcelain dish. If the ore contains sulphur, it is treated with 0·3—0·5 gram potassium chlorate, 10 c.c. of fuming nitric acid are added, and the mixture is heated for one hour. The solution is then diluted with water, allowed to cool, treated with 6 c.c. of sulphuric acid, and heated to expel the nitric acid. Water is again added, and the solution filtered. In the filtrate, the copper is precipitated with sodium thiosulphate. The precipitate is dried, ignited, dissolved in nitric acid, and the copper deposited by electrolysis. D. B.

**Electrolytic Production of Metals and Chlorine.** By F. FISCHER (*Dingl. polyt. J.*, 256, 26—31).—Referring to the electrolytic treatment of the halogen salts of metals, Höpner asserts that,



owing to the difficulties presented by polarisation, attempts to apply electricity on a large scale have hitherto been unsuccessful. He proposes to prevent polarisation by the use of depolarising substances, and claims to have succeeded in decomposing chlorides in a practicable manner, the chlorine given off being utilised in various ways. To obtain metallic sodium by electrolysis, salt is fused in a crucible, the bottom of which is covered with a layer of copper or silver, forming the anode, which is connected by an iron or a copper wire with the corresponding pole of a galvanic battery or dynamo-machine. On completing the circuit, by immersing a carbon cathode into the fused chloride, a deposit of metallic sodium is stated to be produced. By taking into consideration the fact that, for every 23 parts of sodium, 63·5 of copper, or 107 of silver, are required, the author thinks that this process cannot be worked with advantage.

Fischer has continued his experiments on the electrolytic production of magnesium from carnallite. For the details of these experiments, the original paper should be consulted. D. B.

**Production of Platinum in Russia.** (*Dingl. polyt. J.*, 255, 489.)—It is stated that platinum was discovered by accident in the process of gold-washing at Werch-Issetsk in the Ural mountains in 1822. According to Köppen, however, the discovery of platinum appears to have been made at Newjansk in 1819. The extraction was commenced in 1825, 10 puds (1 pud = 16·38 kilos.) being obtained. In 1830, the quantity rose to 106 puds, and in 1840 it reached a maximum, namely 213 $\frac{3}{4}$  puds. The large increase in 1840 was due to the introduction of the platinum coinage. The production fell as soon as the coining of platinum money was abandoned. The following quantities were obtained between 1860 and 1881:—

1860.	1862.	1867.	1870.	1871.	1872.	1873.	
61·5	142·5	109	118	125	93	96 puds.	
1874.	1875.	1876.	1877.	1878.	1879.	1880.	1881.
122	94	96	105	126	138	179	182 puds.

The district of Gloroblagodatski and the works at Nishne-Tagilsk are the centres of the platinum production. D. B.

**Specific Influence of Acetic Acid on the Fermentation of Must, and the Composition of the Wine Produced.** By M. BARTH (*Bied. Centr.*, 1885, 274).

**Abnormal Fermentation under Unfavourable Circumstances, and its Influence on the Composition of the Wine.** By M. BARTH (*Bied. Centr.*, 1885, 275—277).

**Kephir.** By C. HACCIVS (*Bied. Centr.*, 1885, 265—270).—This drink, prepared by the addition of kephir ferment to milk, consists (three days old) of—

Casein.	Albumin.	Peptones.	Total albuminoïds.	Sugar.	Alcohol.	Lactic acid.
2·567	0·7680	0·0222	3·3572	1·5376	1·5° Tr.	1·3500

Nearly all the milk-sugar (5.9582 per cent.) is transformed into lactic acid and alcohol. The casein is in fine flocks, and is partly converted into peptone (hæmialbuminose). E. W. P.

**Extraction of Sugar from Molasses.** By DAIK and POSSOZ (*Dingl. polyt. J.*, 256, 48).—On adding 100—120 parts of lime to 100 parts of the sugar in saccharine solutions containing from 18 to 20 per cent. of sugar, the mixture remains sufficiently fluid, at 0° to 15°, to be forced through filter-presses. On treating solutions of exosmose-molasses in a similar manner, a gelatinous mass is obtained which refuses to pass through the filter-cloth. At 40°, however, the mass becomes more fluid, whilst at 60—120° it is completely liquid and remains fluid, a granular precipitate being produced which can be filtered and washed without difficulty. The precipitate is a peculiar form of a calcium saccharate, to which the authors have assigned the name of osmotic calcium supersaccharate. The production of this saccharate is recommended, in order to obtain the highest yield of sugar from molasses. D. B.

**Turkestan Manna.** By V. MARKOWNIKOFF (*J. Russ. Chem. Soc.*, 1884 [2], 300).—This manna, secreted by a graminaceous plant, *Alhagi maurorum*, or *camelorum*, is used by the natives as a surrogate for sugar, and known under the name *tarondjabin*. The crude product was crystallised by evaporation of its aqueous solution at the ordinary temperature. The crystals proved to be a saccharose, not reducing Fehling's solution, and decomposed by acids, yielding an uncrystallisable glucose, which strongly reduces cupric oxide. It is considered by the author as identical with melezitose (*Beilstein, Handb. org. Chemie*, 578, 1st ed.). The crystals contain 1 mol. H<sub>2</sub>O, which they lose at 100°. It melts at 140°. The rotatory power was found to be  $[\alpha]_D = +88.07$ . It seems to follow from these results that Turkestan manna is identical with the Persian one analysed by Villiers (*loc. cit.*). A. T.

**Preparation of Organic Anhydrides.** (*Dingl. polyt. J.*, 256, 144.)—According to the *Chemische Fabrik, vormals Hoffmand und Schoetensack*, acetic anhydride is obtained by placing 250 kilos. of carefully dehydrated sodium acetate in a cast-iron jacketed agitating vessel, heated at 140°, and passing a current of carbonyl chloride through the mass. A crude oil distils over, which is condensed, and subjected to fractional distillation. It yields 100 kilos. of practically pure acetic anhydride.

For the production of propionic anhydride, sodium propionate is treated with carbonyl chloride at 170°. The distillate consists of propionic anhydride and chloride, and is subjected to fractional distillation for the purpose of separation. The chloride is formed according to the equation  $(C_2H_5 \cdot CO)_2O + COCl_2 = CO_2 + 2C_2H_5 \cdot COCl$ . The preparation of butyric anhydride is effected in a similar manner at a temperature of 200°. A mixture of butyric anhydride and chloride is produced, from which the anhydride is isolated by fractional distillation. When the chloride is distilled over sodium butyrate, free butyric anhydride is obtained.

Benzoic anhydride is prepared by passing carbonyl chloride over sodium benzoate at  $360^{\circ}$ . On distillation, the largest portion of the distillate comes over at  $198^{\circ}$ , and the smallest portion at  $360^{\circ}$ . The former is liquid, and constitutes benzoyl chloride, whilst the latter solidifies to a crystalline mass, melting at  $40^{\circ}$ , and represents benzoic anhydride.

D. B.

**Creaming of Milk.** By W. FLEISCHMANN and J. BERENDES (*Landw. Versuchs-Stat.*, **31**, 366—389).—These experiments, undertaken to determine the relationship between the fat in the skim and whole milk, Laval's centrifugal separator being employed to remove the cream, are most fully detailed, and many tables given. The results obtained so far show that the amount of fat in the skim milk is inversely proportional to the square of the number of rotations per minute, and directly proportional to the quantity of milk creamed. It was hoped that a definite relationship between the percentage of fat in the skim milk and the temperature would have been established. It was, however, observed that the percentage fell with rise of temperature.

E. W. P.

**Preparation of Cheap Cocoa-nut Toilet Soaps.** By F. EICHBAUM (*Dingl. polyt. J.*, **256**, 47).—The author discusses the so-called filling of soaps made from cocoa-nut oil. Soaps charged with soluble glass, although at first exhibiting a fine transparent appearance, gradually dry up and become coated with a solid crust; moreover, such soaps act injuriously on the skin. Salt solutions of  $15$  to  $20^{\circ}$  B. are occasionally used in conjunction with soluble glass. The behaviour of potash solutions is similar to that exhibited by soluble glass. Talc is used either alone or in admixture with soluble glass for the filling of inferior toilet soaps. When it is employed, it is mixed with a small quantity of cocoa-nut oil, and then added to the whole charge of oil.

D. B.

**Curd Soaps.** By F. EICHBAUM (*Dingl. polyt. J.*, **255**, 539).—For the preparation of a good curd soap with silvery fracture, the author proposes boiling 700 kilos. of tallow with soda-ley of  $15^{\circ}$  to a clear jelly, and introducing 450 kilos. of palm-nut and 100 kilos. of cocoa-nut oil with the requisite quantity of caustic ley of  $23^{\circ}$ . The mixture is then boiled until a clear jelly free from froth is obtained. After the lapse of two hours, any scum upon the surface is removed, and the product salted or precipitated respectively with salt solution of  $20^{\circ}$  or caustic soda-ley of  $40^{\circ}$ .

D. B.

**Preparation of New Colouring Matters.** (*Dingl. polyt. J.*, **256**, 134—139.)—For the production of a new blue colouring matter from resorcinol, R. Benedikt proposes melting resorcinol with sodium nitrite at  $130^{\circ}$ . The dye separates from the aqueous solution of the melt in the form of dark red flakes which are readily soluble in alcohol, and give a blue colour on treatment with concentrated sulphuric acid. When heated with zinc-dust and an alkali, the colour is reduced, but reappears on exposing the filtered solution to the air. By this property, the colouring matter is distinguished from Weselsky's diazoresorcinol,

which on reduction and subsequent oxidation forms diazo-resorufin. This dye gives a carmine solution having a vermilion fluorescence.

In order to prepare  $\beta$ -naphthoquinolinesulphonic acid,  $C_{13}NH_5 \cdot SO_3H$ , Gentil recommends heating  $\beta$ -naphthylaminesulphonic acid with glycerol, nitrobenzene, and concentrated sulphuric acid. The excess of nitrobenzene is expelled by steam, the mass converted into the barium salt, filtered, and the barium precipitated by the addition of sulphuric acid. On evaporating the filtrate,  $\beta$ -naphthoquinolinesulphonic acid is deposited. It crystallises in slender white needles. By fusing the acid with potash, the yellow  $\beta$ -hydroxynaphthoquinoline,  $C_{13}NH_5 \cdot OH$ , is obtained.

In order to prepare quinolinedisulphonic acids La Coste proposes heating the two isomeric quinolinemonosulphonic acids (obtained by treating quinoline with fuming sulphuric acid) with twice the weight of fuming sulphuric acid at  $200-240^\circ$ . On fusing the salts of the resulting quinolinedisulphonic acids with about 3 parts of potash or soda at  $180-200^\circ$ , the corresponding salts of hydroxyquinolinedisulphonic acids are obtained. In order to produce dihydroxyquinolines, a larger proportion of alkali is required, and the melt is heated at  $290-310^\circ$ .

For the preparation of quinaldinemonosulphonic acids, according to the *Chemische Fabrik, vormals E. Schering*, quinaldine is introduced into 10 parts fuming sulphuric acid, and the mixture heated at  $100-150^\circ$ . Three isomeric sulphonic acids are produced, the ortho- and para-sulphonic acids being formed at a low temperature, and the  $\beta$ -sulphonic acid, which is the primary product, at the high temperature. The latter is sparingly soluble in water, the ortho-acid dissolves more readily, whilst the para-sulphonic acid is the most soluble. On fusing the ortho-acid with potash, orthohydroxyquinaldine melting at  $74^\circ$  is obtained; the para-acid when similarly treated gives parahydroxyquinaldine melting at  $213^\circ$ , whilst the  $\beta$ -sulphonic acid forms hydroxyquinaldine melting at  $230^\circ$ .

In order to prepare azo-dyes, the *Verein chemischer Fabriken in Mannheim* proposes to expose 1 mol. tetrazoditolyldisulphonic acid to the action of 2 mols. of a phenol dissolved in alkali. Thus, from phenol, cresols, and xlenols yellow dyes are obtained, whilst resorcinol gives orange-coloured dyes, and  $\alpha$ - and  $\beta$ -naphthol and their sulphonic acids red dyes.

According to the *Farbwerke, vormals Meister, Lucius, und Brüning*, azo-colours soluble in alcohol are converted into insoluble compounds by acting on them with bisulphites.

D. B.

**New Series of Dyes.** By O. N. WITT (*Ber.*, 18, 1119—1121).—A series of induline-like dyes are formed by treating the orthazo-derivative of paratoluidine (melting at  $118.5^\circ$ ) (*Abstr.*, 1884, 742) with the hydrochlorides of the primary aromatic bases. The reaction is complicated, and resembles that which takes place in the formation of indulines by the action of aniline hydrochloride on amidobenzene. On heating  $\alpha$ -naphthylamine hydrochloride with orthazoparatoluidine, a compound,  $C_{21}H_{18}N_4$ , is obtained, having, however, no resemblance to the indulines; it forms a bright red crystalline powder, and may be

crystallised from aniline in the form of brilliant yellow needles. Its alcoholic, and especially its ethereal solutions, exhibit a fine green fluorescence. Concentrated sulphuric acid dissolves it with a clear red colour, changing to black, then to green, and lastly to red, on gradual dilution with water. The hydrochloride forms red felted needles of bronze-like lustre, the sulphate forms a sparingly soluble crystalline precipitate. Both salts are soluble in dilute sulphuric acid, forming brilliant red solutions which dye fabrics a fine scarlet; by washing with soap, the colour is changed to yellow. Alkalis precipitate the base from solutions of its salts in amorphous sulphur-yellow flocks, fuming sulphuric acid converts the base into a sulphonic acid, the sodium and barium salts of which were prepared; the free acid in an acetic acid bath dyes silk a fine orange colour. The acetyl compound crystallises in pale yellow silky crystals. Judging from its percentage composition, this base resembles the saffranine-like derivative of orthotoluenediamine, which it also resembles in some of its reactions. The above reactions are common to all the amidazo-compounds in which the amidogen-group is in the ortho-position relatively to the azo-group; they take place with all the amidazo-compounds derived from  $\beta$ -naphthylamine as well as the chrysoïdines; they will, therefore, furnish useful tests for the examination of amidazo-compounds.

A. P.

**Fixing Artificial Colouring Matters by Means of Ferro- and Ferri-cyanides.** By C. REBER (*Dingl. polyt. J.*, 256, 42).—Having found that artificial dyes constituted like amines are precipitated by potassium ferro- and ferri-cyanide, the author recommends the employment of these salts for fixing artificial colouring matters (aniline-violet, magenta, methylene-blue, &c.) on vegetable fibres. He also uses these compounds in the form of insoluble salts of the heavy metals, especially the ferro- or ferri-cyanide of zinc for mordanting purposes.

D. B.

**Tannin-yielding Substances and their Application.** By C. COUNCLER and others (*Dingl. polyt. J.*, 255, 483—488).—According to Councler, mimosa bark from Tasmania (I and II) and Portland in Victoria (III and IV) gave by analysis—

	I.	II.	III.	IV.
Solid matter . . . . .	88.65	91.75	88.25	90.75
Tannin readily soluble . .	15.05	19.93	16.54	12.70
Tannin sparingly soluble	3.83	3.18	4.66	3.60

The bark of *Quercus castanea*, which is brought into Europe from North America in the form of compressed bales, contains from 8 to 9 per cent. of tannin. The coarse bast fibres contains 4.73 per cent. of tannin, which was readily soluble, and 1.92 per cent. of sparingly soluble tannin; the finer particles show 86.5 per cent. of solid matter and 9.35 per cent. of total tannin.

The bark of the stem as well as the roots of the kermes oak (*Quercus coccifera*), cultivated in the south of France and the north of Africa, is largely employed as a tanning agent. The bark of the roots

is known under the name of *Garouille* or African bark. It contains in an air-dried condition 90 per cent. of solid matter, 7·88 per cent. of soluble, and 0·81 per cent. of sparingly soluble tannin.

Birch-bark from Friedrichsrub contains 3·98 per cent. of soluble and 0·97 per cent. of difficultly soluble tannin.

Alder-bark from the province of the Riesenthal has the following composition. 100 parts contain—

Time of felling.	Age in years.	Air-dried substance.				Dry matter.		
		Dry matter.	Tannin.			Tannin.		
			Readily soluble.	Sparingly soluble.	Total.	Readily soluble.	Sparingly soluble.	Total.
May, 1882 .	39	82·00	11·15	0·53	11·68	13·60	0·65	14·25
Dec., 1882 .	39	89·30	5·35	2·03	7·38	5·99	2·27	8·26
May, 1883 .	39	93·20	6·02	2·15	8·17	6·46	2·31	8·77
„ 1882 .	19	89·50	11·82	0·71	12·53	13·21	0·79	14·00
„ 1883 .	19	88·33	8·93	2·22	11·15	10·11	2·51	12·62

Russian willow-bark from one year old osiers contains in 100 parts—

Bark of <i>Salix</i>	Air-dried substance.				Dry matter.		
	Dry matter.	Tannin.			Tannin.		
		Readily soluble.	Sparingly soluble.	Total.	Readily soluble.	Sparingly soluble.	Total.
Purpurea .....	92·2	0·86	0·86	1·72	0·93	0·93	1·86
Viminalis ..	92·1	2·14	1·28	3·42	2·32	1·39	3·71
Purpurea × viminalis.....	91·3	2·70	2·01	4·71	2·96	2·20	5·16
Capisca .....	86·6	1·34	1·28	2·62	1·60	1·53	3·13
Amygdalina .....	92·5	2·27	0·90	3·17	2·45	0·97	3·42

Eitner has examined a large number of samples of Austrian gallnuts of the year 1884, in which a good yield was obtained. The percentage of tannin found in the various specimens ranged between 28·51 and 35·02. The samples contained about 12 per cent. of moisture.

In the *Gerber-Zeitung*, 1884, 275, Counciler makes some important observations as to the comparative value of commercial tannin-yielding substances and extracts prepared therefrom. Specimens of red

quebracho wood (*Loxopterygium Lorentzi*) gave the following numbers on analysis :—

Source.	Tannin.			Dry matter.
	Readily soluble.	Sparingly soluble.	Total.	
Fahr Bros. of Pirmaseus .....	9·20	8·60	17·80	88·7
	9·05	7·59	16·64	90·0
	7·96	9·18	17·14	88·5
	7·66	8·76	16·42	87·5
"Flora," Actiengesellschaft für Farbholzfabrikate, Hamburg. ....	9·24	10·10	19·35	88·0
	10·97	8·39	19·36	90·0
	10·21	7·96	18·17	89·5
	7·96	9·25	17·21	87·5
Bolzmann and Bösenberg, Hamburg ....	8·39	9·89	18·28	88·0

100 kilos. cost from 16 to 18 shillings, so that the cost of 1 kilo. of tannin is less than 1 shilling. It appears that one half of the tannin in quebracho wood liquor is present in a sparingly soluble form. To utilise the whole of the tannin, exhaustion with hot water is recommended. Quebracho extract (solid) contained from 53·6 to 60·2 per cent. of tannin, liquid extract 36·3 per cent. 1 kilo. of the tannin costs 1·2 to 1·5 shillings. Hungarian pine-bark contained 9·33 per cent. of soluble and 3·13 per cent. of difficultly soluble tannin. 100 kilos. of bark are sold at about 11 shillings, so that the tannin costs 1 shilling per kilo. Pine-bark extract contained only 14·12 per cent. of tannin, 100 kilos. cost 43 shillings, equal to 3·05 shillings per kilo. of tannin. The tannin in oak extract, of which 100 kilos. are sold at 55 shillings, costs 3·22 shillings per kilo. Air-dried chestnut wood contained 92·89 per cent. of dry substance, 5·48 per cent. of soluble, and 3·01 per cent. of difficultly soluble tannin, and costs 8 shillings per 100 kilos., equal to 0·94 shilling per kilo. of tannin. Extract of sumach contained 30·1 to 30·3 per cent. of tannin, liquid extract of 30° B. 11·55 per cent. 100 kilos. of extract cost 92 shillings, so that 1 kilo. of tannin costs 4·50 shillings. Alder wood contains 0·43 per cent. of tannin, and mountain-ash wood only 0·17 per cent. These woods are not suitable for the preparation of tannin extracts. The same applies to pines. The cones of *Pinus maritima* contain 0·22 per cent. of soluble and 1·02 per cent. of sparingly soluble tannin, those of the common pine (*Pinus sylvestris*) 1·13 per cent. of sparingly soluble tannin.

Simand (*Gerber*, 1884, 54 and 173) has determined the quantity of extract which it is possible to obtain from a number of tannin-yielding substances. The results are tabulated in the original paper.

Eitner found that commercial oak extract is often adulterated with extract from chestnut wood, or wholly prepared therefrom.

D. B.

## General and Physical Chemistry.

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**A New Order of Metallic Spectra.** By L. DE BOISBAUDRAN (*Compt. rend.*, 100, 1437—1440).—When in observing the spark spectra of solutions of metals of the didymium and yttrium families, the liquid itself is made the positive pole, the upper surface of the liquid becomes luminous and gives a spectrum consisting of several nebulous but sometimes brilliant bands lying between 6205 and 4765. This spectrum could not be traced to any of the known cerite metals, and the author was unable to obtain it with solutions of yttrium compounds. It is, however, identical with the bands given by the phosphorescence of pure yttrium compounds as observed by Crookes in high vacua. The direct contradiction between these observations is at present the subject of further experiments.

C. H. B.

**Absorption Spectrum of Nitrogen Peroxide.** By L. BELL (*Amer. Chem. J.*, 7, 32—34).—The author concludes from his experiments on the absorption spectrum of nitrogen peroxide at different temperatures, that the absorption is entirely due to that part of the gas in the form of the molecule  $\text{NO}_2$ , whilst that portion in the molecular form  $\text{N}_2\text{O}_4$  does not produce any absorption spectrum at all.

A. J. C.

**Relation between the Composition and the Absorption Spectra of Organic Compounds.** By G. KRÜSS (*Ber.*, 18, 1426—1433).—Krüss and Economides examined (*Abstr.*, 1883, 1041) solutions of indigo and its derivatives, with a view to decide whether the replacement of hydrogen in a compound by Me, Et, NO,  $\text{NH}_2$ , Br, &c., has a regular influence on the absorption spectrum of the compound. The author has now examined the absorption spectra of aqueous and alcoholic solutions of fluoresceïn, dibromofluoresceïn, tetrabromofluoresceïn together with its metallic derivatives, tetranitrofluoresceïn, dibromodinitrofluoresceïn, methyltetrabromofluoresceïn, ethyltetrabromofluoresceïn, rosolic acid, and tetrabromorosolic acid, both with and without the addition of alkali.

The results confirm the view previously (*loc. cit.*) brought forward, that the replacement of hydrogen in the benzene-ring or in the side-chain by methyl, oxymethyl, ethyl, and bromine, causes a shifting of the absorption towards the less refractive end of the spectrum, whilst the introduction of an amido- or nitro-group has the opposite effect. This shifting increases proportionally to the number of hydrogen-atoms when the same elements or groups are substituted analogously.

N. H. J. M.

**Refractive Power of Chemical Compounds.** By J. KANONNIKOFF (*J. pr. Chem.* [2], 31, 321—363).

**Calorimetric Researches.** By M. RUBNER (*Zeit. f. Biol.*, 21, 250—334 and 337—410).



**Heat of Formation of Ferrous Sulphide.** By R. MÜLLENHOFF (*Ber.*, 18, 1365—1366).—This is the description of a simple method, by which the heat of formation of ferrous sulphide may be practically demonstrated as a lecture experiment. A. P.

**Apparatus for Fractional Distillation under Reduced Pressure.** By A. GORBOFF and A. KESSLER (*Ber.*, 18, 1363—1364).

**New Thermo-regulator.** By A. FOCK (*Ber.*, 18, 1124—1126).

**Fractional Distillation in a Current of Steam.** By F. RASIŃSKI (*J. pr. Chem.* [2], 31, 428—436).—The author, in the course of investigations on the fractional distillation of Baku petroleum in a current of steam (*Abstr.*, 1884, 936), has confirmed Mendelejeff's observation on the periodic rise and fall of the curve of distillation, in which the abscissæ are the relative volumes of oil and water distilled over, and the ordinates the corresponding sp. gr. This periodic rise and fall occurs at equal intervals along the ordinate axis, and before each period there is observable an increase of fraction of the distillate. These phenomena are illustrated in the original paper by a series of tables. V. H. V.

**Density of Sulphurous Anhydride at a White Heat.** By C. LANGER and V. MEYER (*Ber.*, 18, 1501—1504).—In these experiments, the apparatus was charged with nitrogen and a constant temperature having been attained, a measured volume of sulphurous anhydride was passed in. On measuring the displaced nitrogen, the following results were obtained:—

	I.	II.	III.
Sulphurous anhydride used..	1.70 c.c.	1.75 c.c.	2.35 c.c.
Nitrogen displaced .....	1.60 „	1.65 „	2.25 „

showing that sulphurous anhydride and nitrogen expand to nearly the same extent at a white heat. No change in the gas could be detected qualitatively, but it is possible that dissociation may have taken place to a small extent; this would account for the slight deficiency of nitrogen, as it is known that platinum can absorb traces of oxygen, and most probably it would also take up sulphur at the temperature employed.

Experiments with oxygen and nitrogen had previously shown that these two gases expand to an equal extent, and from this it is concluded that their coefficient of expansion at the temperature employed is the same as that of all normal gases at low temperatures. Carbonic anhydride gave practically the same result, although dissociation could be detected to a minute extent. The temperature in these experiments was registered by means of a nitrogen thermometer and found to be 1690°. A. K. M.

**Estimation of the Specific Gravity of Liquids at Higher Temperatures.** By R. SCHIFF (*Ber.*, 18, 1538—1540).—For this purpose the author employs a pear-shaped flask completely filled with

the liquid under examination, and heated by being surrounded by the vapour of a liquid of known boiling point. During the heating, an accurately ground hollow stopper is attached to the capillary neck of the flask, in which the liquid expelled collects and cannot re-enter the flask on cooling. By choice of a series of liquids of increasing boiling points, successive determinations of the sp. gr. of a liquid at various temperatures are quickly made. The determination of the volume and expansion coefficient of the flask is best effected by determining the weight of mercury contained at the ordinary temperature, and after heating in ether vapour and in steam. A. J. G.

*Note.*—A somewhat similar application of the principle of the weight thermometer, but only suited to the determination of the sp. gr. of a liquid at its own boiling point, was described by Ramsay (*Trans.*, 1879, 466).

**Motions of Camphor on the Surface of Water.** By T. HART (*Chem. News*, 51, 277—278).—Casamajor (*ibid.*, 109) attributes these motions to the facts that the specific gravity of camphor is lower than that of water, and that camphor is soluble in water. The author considers both these improbable as causes of the phenomenon, and suggests the following explanation. The cohesion of camphor being small, and its adhesion for water being great, camphor tends to spread itself over the surface of water, in doing so the particles are kept in constant motion, and they in their turn give motion to the mass. Experiments are adduced in support of this suggestion, and substances with similar properties, such, for instance, as collodion, are observed to behave in a similar manner. D. A. L.

**Action of some Metals on Mixtures of Acetylene and Air.** By F. BELLAMY (*Compt. rend.*, 100, 1460—1461). When a spiral of platinum or silver wire heated just to incipient redness is brought into a mixture of acetylene and air issuing from a modified Bunsen burner made of glass, the gaseous mixture at once detonates and inflames, but the spiral does not become incandescent. If, however, a copper spiral is treated in the same way, the wire becomes brilliantly incandescent, and eventually ignites the gaseous mixture. A spiral of iron wire behaves in a similar manner, but the incandescence is more difficult to obtain; if the spiral is too hot, the gaseous mixture is at once ignited, if too cold the wire remains non-luminous.

Copper or iron wire does not become incandescent in a mixture of air and hydrogen. C. H. B.

**New Method for Determining the Size of Molecules.** By F. EXNER (*Monatsh. Chem.*, 6, 249—278).

**Apparatus and Arrangements of the Laboratory at Dresden.** By W. HEMPEL (*Ber.*, 18, 1434—1440).—The following are described with sketches: filter-press, draught arrangement for poisonous gases, apparatus for the preparation of hydrofluoric and hydrofluosilicic acids, apparatus for the evolution of oxygen. N. H. J. M.

## Inorganic Chemistry.

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**Composition of Hydrogen Persulphide, and a Nacreous Variety of Sulphur.** By P. SABATIER (*Compt. rend.*, 100, 1346—1347).—Hydrogen persulphide carefully prepared by Thenard's process, and well dried, was introduced into a distillation apparatus consisting of a small flask with a short neck, furnished with a bulb tube which was surrounded by ice and connected with an air-pump. When the pressure was reduced to 0.04—0.1 m., and the contents of the flask heated to 60—85° in a water-bath, the hydrogen persulphide distilled regularly. Towards the close of the operation the temperature was raised to about 90°, and the drops which formed in the neck of the apparatus became yellowish. The distillate obtained in this way is a brilliant, pale yellow, very limpid, mobile liquid with an extremely irritating odour. The analytical results agree with the formula  $\text{H}_2\text{S}_5$ , but the true composition of hydrogen persulphide is probably  $\text{H}_2\text{S}_2$ , the excess of sulphur being due to the decomposition which takes place in the early stages of the operation, and to sulphur carried over mechanically.

When hydrogen persulphide is brought in contact with ethyl ether in a closed vessel, somewhat large, nacreous lamellæ of sulphur are deposited in a short time. The same reaction takes place somewhat more slowly with ethyl acetate, and still more slowly with ethyl or amyl alcohol. This nacreous variety of sulphur has already been described by Gernez. It rapidly changes into the octahedral variety, especially in contact with already formed octahedra. Hydrocarbons and derivatives such as chloroform, do not give this reaction with hydrogen persulphide.

C. H. B.

**Rate of Transformation of Prismatic into Octahedral Sulphur.** By D. GERNEZ (*Compt. rend.*, 100, 1343—1345 and 1382—1385). The author has previously described the phenomena which accompany the conversion of superfused sulphur into the prismatic variety under varying conditions (*Abstr.*, 1884, 389, 553, and 889), and he has now investigated in a similar manner the inverse changes of prismatic sulphur into the octahedral variety. Sulphur kept in superfusion at 97° in glass tubes, was converted into the prismatic variety in the manner already described (*loc. cit.*), and the solid prismatic sulphur was then carefully touched with an octahedral crystal. The conversion of the prismatic into the octahedral variety commences at once, and gradually extends throughout the whole length of the tube, the progress of the change being easily traced by the loss of translucency. Other conditions being the same the change progresses through equal distances in equal intervals of time, and the rate at which the change travels may be termed the *velocity of devitrification of prismatic sulphur*. The change takes place the more slowly the nearer the temperature approaches to 97°, at which point the change is impossible. It takes place more rapidly the lower the temperature, down to 54.7°, but beyond this point a decrease in the

temperature diminishes the velocity of devitrification. The temperature most favourable to the change is  $44-55^{\circ}$ . The velocity of devitrification is greater the lower the temperature at which the prisms were formed, and also increases with the time during which the sulphur was kept in superfusion. This latter influence disappears, however, when the time of superfusion is very long, the rate of change being the same whether the sulphur was kept in superfusion for four or for six hours. The velocity of devitrification is very considerably diminished if the sulphur is originally fused at a temperature much above its melting point, and the same result is brought about by keeping the sulphur in a state of fusion for a long time, even though the temperature is not far above the melting point. Under certain conditions the rate of devitrification may be extremely slow even though the change takes place under the most favourable conditions of temperature. In all these experiments the sulphur was initially in the form of octahedra which had not been fused. Any previous fusion or crystallisation exerts a marked effect on the behaviour of the sulphur under different conditions, and many successive fusions, crystallisations, and devitrifications are necessary to bring the sulphur into a molecular condition characterised by a constant velocity of devitrification.

C. H. B.

**Volatility of Sulphur and Mercury.** By BERTHELOT (*Compt. rend.*, 100, 1326—1328).—When gunpowder is dried in the usual way at  $60-65^{\circ}$  a peculiar odour is observed. This smell is due to the sublimation of sulphur, which also carries with it small quantities of the non-volatile constituents of the gunpowder. A quantity of the sublimate, condensed and collected on sheets of glass, had the composition: sulphur 97.84, potassium nitrate 0.90, charcoal, &c.,  $1.26 = 100$ . The vapour-tension corresponding to this sublimation is too small to be measured.

A bottle of iodine standing about 2.5 metres from a vessel containing mercury was observed after a long time to be covered with scarlet mercuric iodide round the stopper. This fact would seem to show that the vapour which is given off from mercury at the ordinary temperature has considerable power of diffusion, although its tension is extremely low.

C. H. B.

**Sulphurous Anhydride in the Air of Towns.** By G. WITZ (*Compt. rend.*, 100, 1385—1388).—The existence of sulphurous anhydride as a normal constituent of the air of towns is shown by the fact that placards coloured with red lead, posted in situations where they are protected from the sun and rain, become gradually decolorised, whereas similar placards exposed under similar conditions in country air retain their colour unimpaired. The decolorised placards are found to contain lead sulphate and lead sulphite, the lead dioxide in the red lead having been converted into the former, and the monoxide into the latter. This decolorisation of the red lead takes place much more rapidly in shop windows where gas is burnt. The author has also frequently been able to recognise sulphurous acid in hail, snow, and especially hoar frosts in the neighbourhood of towns.

The presence of sulphurous anhydride is undoubtedly one of the most important causes which diminish the amount of ozone in the air of towns.

A delicate test for a sulphite consists in adding to the substance some very dilute acid, a fragment of zinc, and a small quantity of indigo solution. In presence of a sulphite the indigo is decolorised, owing to the production of hyposulphite. C. H. B.

**Nature of Selenium Sulphide and of Alloys.** By R. RATHKE (*Ber.*, 18, 1534—1538).—The author dissents from the view expressed by Divers and Shimidzu (*Trans.*, 1885, 446) that the only compound of selenium and sulphur known as yet is selenium monosulphide, and considers that he has brought forward sufficient evidence to show that other compounds do exist, although not yet isolated in a pure state. He suggests that closely allied elements, or elements having but a feeble attraction for one another, can combine in several proportions to form products of the same crystalline form, citing the crystalline alloys of zinc and antimony obtained by Cooke, in which the zinc varied from 43 to 55 per cent. without altering the crystalline form.

A. J. G.

**Solubility of Nitric Oxide in Sulphuric Acid.** By G. LUNGE (*Ber.*, 18, 1391—1394, and *J. Soc. Chem. Ind.*, 1885, 447).—Allen has pointed out (*ibid.*, 178) that in working with the author's nitrometer, a layer of froth is frequently formed at the contact of the mercury and acid, and also at the surface of the acid itself. These layers of froth may be avoided in the first case by allowing the liquids full time to cool to the temperature of the air before measuring, and in the second by carefully greasing the stopcock and the mouth of the tube with the least possible quantity of vaseline.

Allen also states that a considerable error is introduced by the solubility of nitric oxide in concentrated sulphuric acid, and he advises that the loss in this way should be estimated after measuring the gas by diluting the sulphuric acid with one-half its bulk of water, when the nitric oxide is given off and may be measured. This, however, is not the case, as is shown by the following experiments:—

1st. Sulphuric acid, sp. gr. 1·84, which had been saturated with nitric oxide at 18° and 760 mm., was titrated with a standard solution of potassium permanganate, the acid solution of nitric oxide being carefully preserved from any contact with the air. 1 c.c. of this acid was found to contain 0·035 c.c. of nitric oxide. A second experiment was made in the same way with an acid of 1·50 sp. gr. made by diluting the strong acid with an equal bulk of water; it was found that 1 c.c. contained 0·017 c.c. of nitric oxide, therefore by diluting an acid of 1·84 sp. gr., saturated with nitric oxide with an equal volume of water, only 0·0001 c.c. of nitric oxide will be given off; from this it is clear that the correction for the absorption of nitric oxide in the sulphuric acid cannot be made by diluting the acid, and in fact the whole error introduced by this absorption is so small that for all ordinary experiments it may be safely neglected.

A. P.

**Combination of Bromine with Phosphorus Trifluoride.** By H. MOISSAN (*Compt. rend.*, **100**, 1348—1350).—When carefully dried phosphorus trifluoride is passed into dry bromine cooled in a freezing mixture, an amber-coloured, very mobile liquid is obtained, which fumes strongly in the air and is violently decomposed by water with formation of hydrobromic, hydrofluoric, and phosphoric acids. When cooled below  $-20^{\circ}$  the liquid deposits pale-yellow crystals which quickly melt when taken from the freezing mixture.

The liquid has the composition  $\text{PF}_3\text{Br}_2$ , and at the ordinary temperature it gradually and somewhat rapidly decomposes into phosphorus pentafluoride and yellow or red crystals of phosphorus pentabromide, in accordance with the equation  $5\text{PF}_3\text{Br}_2 = 3\text{PF}_5 + 2\text{PBr}_5$ .

C. H. B.

**Compounds of Arsenious Oxide.** By F. RÜDORFF (*Ber.*, **18**, 1441).—Schiff and Sestini have recently examined the compounds which arsenious oxide forms with potassium iodide and bromide (this vol., p. 723), but they were unable to obtain the corresponding compound with potassium chloride. This may be obtained as a crystalline powder when a solution of potassium chloride (10 grams) and potassium arsenite (50 grams) in warm water (200 c.c.) is left to cool slowly; also by mixing a 10 per cent. solution of the chloride with a 50 per cent. solution of the arsenite. It forms hexagonal scales of the formula  $2\text{KCl} \cdot 2\text{As}_2\text{O}_3 + \text{H}_2\text{O}$ . The compounds with potassium bromide and iodide may be obtained in the same way and crystallise in hexagonal scales and prisms respectively.

A. K. M.

**Sulphides of Cerium and Lanthanum.** By P. DIDIER (*Compt. rend.*, **100**, 1461—1463).—A current of dry hydrogen sulphide was passed over cerosoceric oxide heated in a porcelain or carbon dish in a porcelain tube. The reaction commences below the melting point of glass. The sulphide obtained is vermilion or black according to the temperature. It forms a porous mass of sp. gr. 5.1, and seems to be infusible. It does not alter when exposed to air at the ordinary temperature, but it burns below a dull red heat with production of sulphurous anhydride and cerosoceric oxide. It has the composition  $\text{CeS}$  if  $\text{Ce} = 94$ , or  $\text{Ce}_2\text{S}_3$  if  $\text{Ce} = 141$ ; is only slowly decomposed by warm water, but dissolves readily even in very dilute acetic acid with evolution of hydrogen sulphide and without precipitation of sulphur. When treated with alkaline sulphides, it undergoes alteration, but does not become crystalline. It can, however, be obtained in red translucent crystals by passing dry hydrogen sulphide over a fused mixture of sodium chloride and anhydrous cerium chloride and extracting the soluble salts with water.

Lanthanum yields a similar compound under the same conditions, but this is yellow and is much more easily decomposed by water.

The readiness with which the cerite metals form sulphides stable in presence of water at the ordinary temperatures distinguishes them from metals of the aluminium-group.

C. H. B.

**Formation of Red Silver Solutions by Reduction.** By O. v. D. PFORDTEN (*Ber.*, **18**, 1407—1408).—From results obtained by

Wöhler (*Annalen*, **30**, 1) it seemed probable that all soluble argentous salts and their solutions would have a red colour. This view is confirmed by experiments described by the author. A concentrated solution of silver nitrate, when treated with phosphorous acid, assumes a red colour which becomes more and more intense until the separation of a black powder (silver or argentous oxide) occurs. The red colour is also produced when a solution of silver nitrate and nitric acid is treated with sulphurous anhydride.

The formation of a red solution from Wöhler's solid salt, and the fact that the solutions remain red in presence of free nitric acid, and give absorption spectra consisting chiefly of a red band without characteristic lines, make it probable that the liquid really is a solution of an argentous salt, and does not contain metallic silver in solution or in suspension. The author intends continuing the investigation, especially with regard to the behaviour of the red solutions towards hydrochloric acid.

N. H. J. M.

**Action of Light on Silver Chloride.** By S. B. NEWBURY (*Amer. Chem. J.*, **6**, 407—411).—The author worked as follows:—In each experiment the quantity of silver nitrate necessary to produce 0.1 gram of silver chloride was dissolved in 100 c.c. of water and a very minute excess of sodium chloride, dissolved in the same quantity of water, added. The finely suspended precipitate was exposed to light for varying periods, a current of air being continually drawn through the liquid to hinder subsidence and carry off any chlorine liberated. The precipitate was then collected on a Gooch filter and dried at 140°. Blank experiments (where light was excluded) yielded 0.0996—0.0997 gram silver chloride. After weighing, the exposed precipitate was treated with hot ammonia and the residual silver weighed. Four experiments, where the exposure was continued for several days, gave—

	Weight of precipitate.	Loss beyond experimental error.	Metallic silver.	Metallic silver calculated from loss.
1.	0.0967	0.0029	0.0054	0.0085
2.	0.0979	0.0018	0.0076	0.0054
3.	0.0969	0.0027	0.0078	0.0081
4.	0.0982	0.0015	0.0062	0.0045

When small quantities of stannous chloride are added to the mixture, before exposure to light, blackening takes place more rapidly and subsidence is much slower and less complete. The grey precipitate obtained consisted almost wholly of finely-divided silver.

All attempts to isolate a subchloride from the blackened silver chloride precipitate proved unavailing. Ammonia, sodium thiosulphate, potassium cyanide, and sodium chloride were employed as solvents for the silver chloride, but in each case metallic silver only was left.

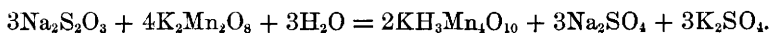
The author also endeavoured to prepare silver subchloride by von Bibra's method (this Journal, 1875, 1162) of reducing silver citrate in hydrogen and treating the residue with hydrochloric acid, but the

resultant compound when treated with a dilute solution of sodium chloride only yielded metallic silver.

The author considers that these results support the view of the non-existence of the subchloride, as otherwise it must be assumed that this subchloride is decomposed into silver and silver chloride by the action of a cold, dilute solution of sodium chloride, which is highly improbable.

L. T. T.

**Action of Potassium Permanganate on Sodium Thiosulphate.** By M. GLÄSER (*Monatsh. Chem.*, 6, 329—333).—According to Morawski and Stingl (Abstr., 1879, 204) potassium permanganate can effect complete oxidation in neutral solutions, and is thereby converted into  $\text{KH}_3\text{Mn}_4\text{O}_{10}$ . On the other hand, it is maintained by Hönig and Zatzek (Abstr., 1884, 151) that this oxidation of sodium thiosulphate can take place in alkaline solutions of potassium permanganate only, and that the manganite formed has the composition  $\text{KH}_3\text{Mn}_3\text{O}_8$ . The author has examined this question, and shows that the potassium carbonate used by the last-named chemists to produce the alkalinity of the solution, has no part in the reaction, that sodium thiosulphate is completely oxidised by a neutral solution of potassium permanganate, and that the manganite,  $\text{KH}_3\text{Mn}_4\text{O}_{10}$ , is formed, thus:—



P. P. B.

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## Mineralogical Chemistry.

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**Chemical Examination of Nocerine.** By E. FISCHER (*Zeit. Kryst. Min.*, **10**, 270—272).—The nocerine examined came from Sarno-Nocera. The analysis gave the following results:—

Al.	Ca.	Mg.	K.	Na.	F.	O.	Total.
4.38	26.92	17.52	0.51	2.47	37.6	11.4	100.80

Subtracting the percentage of Al, K, and Na, the mineral has the formula  $2(\text{CaMg})\text{F}_2 + (\text{CaMg})\text{O}$ . B. H. B.

**The Borax Deposits in California and Nevada.** (*Pharm. J. Trans.* [3], **15**, 874.)

**Borax Deposits.** By H. G. HANKS (*Third Annual Report of the State Mineralogist of California*). This report, which covers 111 pages, contains an exhaustive description of the borax deposits of California and Nevada. B. H. B.

**Colemanite from California.** By C. BODEWIG and G. V. RATH (*Zeit. Kryst. Min.*, **10**, 179—186). The mean of a number of analyses was—

	H <sub>2</sub> O.	CaO.	B <sub>2</sub> O <sub>3</sub> .	Total.
I.	22·26	27·42	49·70	99·38
II.	21·87	27·22	50·91	100·00

II is the theoretical composition corresponding to the formula  $\text{Ca}_2\text{B}_6\text{O}_{11} + 5\text{H}_2\text{O}$ . The crystals are monoclinic; the axial elements being  $a : b : c = 0.7769 : 1 : 0.5416$ . The authors have observed 14 forms, all of which are given in A. W. Jackson's list (Abstr., 1885, 358).

A. Arzruni (*Zeit. Kryst. Min.*, **10**, 272—276), working independently, has observed 20 forms. J. T. Evans (*Zeit. Kryst. Min.*, **10**, 316), the original discoverer of the mineral, gives the following analysis:—

H <sub>2</sub> O.	CaO.	B <sub>2</sub> O <sub>3</sub> .	Total.	Sp. gr.
21·84	27·18	50·98	100·00	2·428

(Compare also Abstr., 1885, 224).

B. H. B.

**Calaite, Pseudomorphous after Apatite, from California.** By G. E. MOORE and V. v. ZEPHAROVICH (*Zeit. Kryst. Min.*, **10**, 240—251).

—The calaite was found by J. D. Whitney in granite at Taylor's ranch, Fresno Co. The measurements of V. v. Zepharovich prove it to have undoubtedly the form of apatite. The mean of four determinations gave  $\alpha c = 40^\circ 35'$ ; and in apatite, this angle is  $40^\circ 18'$ , according to Koksharow, or  $40^\circ$  to  $40^\circ 30'$ , according to Breithaupt. The analysis by G. E. Moore gave the following results:—

Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CuO.	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Total.	Sp. gr.
35·98	2·99	7·80	33·21	19·98	99·96	2·806

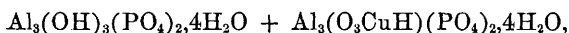
This agrees fairly well with the analysis of calaite from Nichabur, by Church (*Chem. News*, **10**, 290). A characteristic property of calaite is the brown colour it acquires on ignition. In order to determine the relation between this change of colour, and the loss of water, an experiment was made with the following results:—

Colour.	Temperature.	Loss of weight. Grams.	Percentage of water.
White .....	180° C.	0·0248	2·57
Begins to brown .....	Red heat	0·1612	16·72
	Dark-red heat	0·0010	0·10
	Cherry-red heat	0·0013	0·13
	High red heat	0·0021	0·22
Chocolate-brown .....	White heat	0·0034	0·35
		0·1938	20·09

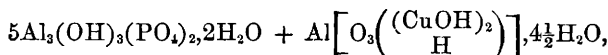
From this, it appears that the dark colour produced on heating is not so dependent on the loss of water as on the formation of a new copper compound by the action of heat. This is confirmed by the

microscopic examination, which shows that the blue colouring copper compound is not uniformly distributed through the calaite, but that it occurs principally in the more central portions of spherulites.

From the analysis, the formula—



is calculated. This formula, however, does not take into account the fact that the cupriferous compound is decomposed more easily by heat than the compound free from copper; this property does not well agree with the theory of two similar phosphates. The analytical results, however, also allow the assumption that a copper aluminate is present with the aluminium phosphate. It is true that up to the present time but one copper aluminate is known, that is the mineral described by Church (this Journal, 1870, 1) as namaqualite. Assuming, then, that the copper is present in the calaite as namaqualite, the formula may be written—



in which the aluminium phosphate has the constitution of wavellite, less  $2\frac{1}{2}$  mols. of water.

B. H. B.

**Manganese Arsenates from Nordmarken in Wermland.** By H. SJÖGREN (*Zeit. Kryst. Min.*, 10, 113—155).—The author describes the four new minerals discovered in 1884 at the Moss mine. Three of these minerals—allactite, diadelphite, and synadelphite—were discovered by H. Sjögren, the fourth—hæmafibrte—by L. J. Ingelström.

*Allactite* is monoclinic, isomorphous with the vivianite and pharmacolite groups.  $a : b : c = 0.6127 : 1 : 0.3338$ .  $\beta = 84^\circ 16'$ . It usually occurs in the forms:  $\infty P\infty$ ,  $\infty P\frac{3}{2}$ ,  $-P\infty$ ,  $+P\infty$ ,  $-4R4$ . It possesses a distinct cleavage parallel to  $-P\infty$ , and less distinct parallel to  $\infty P\infty$ .  $H. = 4.5$ . It has a glassy lustre, is transparent, and strongly trichroic. The usual colours are hyacinth-red and olive-green. The streak is brownish-grey. The mineral is optically biaxial, with negative double refraction. The plane of the optic axes coincides with the plane of symmetry. Sp. gr. 3.8. Analysis gave the following results:—

$\text{As}_2\text{O}_5$ .	MnO.	MgO.	$\text{H}_2\text{O}$ .	Total.
28.76	62.19	0.55	8.97	100.47

corresponding to the formula  $\text{Mn}_3\text{O}_5(\text{AsO})_2 \cdot 4\text{MnO} \cdot \text{H}_2$ . The mineral is easily soluble in acids, and almost infusible before the blowpipe. It occurs with several hydrated manganese arsenates, magnetite, haumannite, and fluor spar, in a limestone vein at the Moss mine.

2. *Hæmafibrte* is rhombic, isomorphous with scorodite and strengite.  $a : b : c = 0.5261 : 1 : 1.1502$ . The forms are:  $\infty P$ ,  $\dot{P}2$ ,  $\infty \dot{P}\infty$ . It occurs but rarely crystallised, usually in drusy cavities filled with radiated aggregates. The cleavage is parallel to  $\infty \dot{P}\infty$  and distinct.  $H. = 3$ . Colour, brownish-red to garnet-red, with vitreous lustre; powder and streak, brick-red; translucent to transparent. The plane

of the optic axes is parallel to the macrodiagonal pinacoid. The primary bisectrix, which is positive, coincides with the vertical axis. Sp. gr. 3.5 to 3.65. Analysis gave the following results:—

As <sub>2</sub> O <sub>3</sub> .	MnO.	FeO.	H <sub>2</sub> O.	Total.
30.76	57.94	0.79	12.01	101.50

corresponding to the formula As<sub>2</sub>O<sub>3</sub>Mn<sub>3</sub>O<sub>6</sub>·3MnO + 5H<sub>2</sub>O. The mineral was found at the Moss mine, where it occurs in a vein of calcite, diallogite, and hausmannite.

3. *Diadelphite* is hexagonal, rhombohedral;  $a : c = 1 : 0.8885$ . Observed forms, +R, +2R, + $\frac{3}{4}$ R, and 0R, with the first-named rhombohedron predominating. H. = 3.5. The colour is brown-red to garnet-red; streak, light chocolate-brown; translucent; optically uniaxial, with negative double refraction. The majority of the crystals, however, exhibit optical anomalies. Sp. gr. 3.3 to 3.4. Analysis gave the following results:—

As <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.	Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Total.
22.54	50.98	0.71	5.38	8.61	14.02	102.24

corresponding to the formula As<sub>2</sub>O<sub>3</sub>(AlFeMn)<sub>2</sub>O<sub>6</sub> + 8MnO<sub>2</sub>H<sub>2</sub>.

4. *Synadelphite* is monoclinic, isomorphous with lazulite and liroconite.  $a : b : c = 0.8581 : 1 : 0.9192$ .  $\beta = 90^\circ 0'$ . The usual forms are  $\infty P \infty$ , + $\frac{1}{2}P \infty$ , - $\frac{1}{2}P \infty$ ,  $\infty R^2$ ,  $\infty R^3$ , +P, -P. Colour, black; streak, light chocolate-brown. H. = 4.5. The plane of the optic axis is perpendicular to the plane of symmetry; axial angle small. Sp. gr. 3.46—3.5. Analysis gave the following results:—

As <sub>2</sub> O <sub>3</sub> .	Mn <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.	H <sub>2</sub> O.	Total.
29.31	11.79	6.16	1.23	35.71	3.76	2.19	11.39	101.54

corresponding to the formula As<sub>2</sub>O<sub>3</sub>(AlFeMn)<sub>2</sub>O<sub>6</sub> + 5MnO<sub>2</sub>H<sub>2</sub>.

B. H. B.

**Mineralogical Notes.** By E. F. SMITH (*Amer. Chem. J.*, **6**, 411—414).—The author has found *pectolite* at Hosensack Station, Lehigh Co., Pa., in grey acicular crystals of sp. gr. 2.6. *Titanite* was also found about two miles from the above spot. Analyses of these minerals are given, as also of the following from new localities: *glauconite* from French Creek, Chester Co., Pa., *heulandite*, *apophyllite* and *menaccanite* near Adamstown, Lancaster Co., Pa., *stilbite* from Rautenbusch and Fegley's Mine, Berks Co., Pa.

L. T. T.

**Synthesis of Anorthite.** By S. MEUNIER (*Compt. rend.*, **100**, 1350—1352).—On taking down one of the furnaces at the gas works at Vaugirard, the stony matter formed by the fusion of the refractory substances composing the bottom of the furnace was found to contain distinct crystals, which in their composition and optical properties are identical with natural anorthite. The stony matter surrounding these crystals was impregnated with microliths of the same mineral, and dark-coloured rhombic tables of pyroxene were also present.

C. H. B.

**Ottrelith Rocks of Ottré and Viel-Salm.** By L. v. WERVEKE  
(*Jahrb. f. Min.*, 1885, **1**, 227—235).

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## Organic Chemistry.

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**Derivatives of Cyanmethine.** By P. KELLER (*J. pr. Chem.* [2], 31, 363—382).—Although cyanmethine, prepared by a method analogous to that for cyanethine (comp. Abstr., 1883, 633) would be considered to be a homologue of it, yet the difference in properties between the two substances is most marked. Thus bromocyanethine is produced only by protracted heating of cyanethine and bromine in sealed tubes, but bromocyanmethine is formed by shaking a hydrochloric acid solution of cyanmethine with bromine; the latter compound forms with nitrous acid the *nitrate* of a *bromoxy-base*,  $C_6H_7BrN_2O, HNO_3$ , which crystallises in long white needles, melting with decomposition at  $158^\circ$ , insoluble in ether, readily soluble in water; the silver salt of the bromoxy-base,  $C_6H_6BrAgN_2O$ , is crystalline. Secondly, with chlorine cyanethine forms trichlorocyanmethine, but cyanmethine under the same conditions gives chlorocyanmethine dichloride,  $C_6H_5ClN_3, Cl_2$ ; the latter substance sublimes at  $200^\circ$ , and readily gives up a molecule of chlorine; with nitrous acid, it forms the nitrate of a chloroxy-base,  $C_6H_7ClN_2O, HNO_3$ , which melts at  $133^\circ$ ; but trichlorocyanmethine gives under the same conditions the nitrate of a trichloroxy-base.

Phenyl cyanate in solution in benzene and cyanmethine, when heated together, combine directly with formation of *carbanilidocyanmethine*,  $PhNH \cdot CO \cdot NH \cdot C_6H_5, N_2$ ; it crystallises in needles melting at  $225^\circ$ ; is readily soluble in benzene, alcohol, and chloroform; with bromine, it forms a dibromo-derivative, an amorphous substance melting at  $238^\circ$ . Similarly phenyl cyanate and monobromocyanmethine form monobromocarbanilidocyanmethine,



crystallising in needles which melt at  $190^\circ$ . The formation of cyanmethine from methyl cyanide and sodium appears to be conditioned by the pressure under which the reaction is effected; thus when methyl cyanide and sodium were heated together in a vessel, connected with a manometer, which showed a pressure of 11 atmos. from the marsh-gas generated, the yield of cyanmethine was satisfactory; but under ordinary pressure, in an atmosphere of carbonic anhydride, no cyanmethine was produced.

V. H. V.

**Action of Chlorine on Isobutyl Alcohol.** By H. BOQUILLON (*J. Pharm.* [5], 11, 654—657).—By the action of chlorine on isobutyl alcohol there are obtained (1) isobutyl chloride, (2) a crystalline substance of the formula  $C_4H_9ClO_2$ , either a chlorisobutaldehyde or more probably a polymeride thereof; it forms long, colourless, acicular

prisms, melts at  $106^{\circ}$ , boils at  $173^{\circ}$ , and is insoluble in water and glycerol, soluble in hot alcohol, carbon bisulphide, light petroleum, &c.; (3) a colourless liquid of the formula  $C_{24}H_{25}ClO_4$ , and of penetrating odour; sp. gr. 0.967 at  $15^{\circ}$ ; it boils at  $184$ – $186^{\circ}$ , is insoluble in benzene, water, and glycerol, sparingly soluble in carbon bisulphide, soluble in alcohol, ether, and chloroform; (4) a liquid boiling at  $216$ – $218^{\circ}$ , and still under investigation. A. J. G.

**Non-acid Constituents of Beeswax.** By F. SCHWALBE (*Chem. Centr.* [3], 16, 354–355).—Beeswax after removal of the cerotic acid was saponified with alcoholic soda, and the dried soap extracted with light petroleum. A mixture of alcohols was obtained, melting after fractionation between  $62^{\circ}$  and  $82^{\circ}$ . From the lower melting portions, two hydrocarbons belonging to the paraffin series were extracted, forming about 5 per cent. of the original wax. From the higher fractions, the alcohol,  $C_{31}H_{64}O$ , melting at  $85^{\circ}$ , was isolated, which, on fusion with soda-lime, yielded a ketone melting at  $97$ – $99^{\circ}$ , and an acid melting at  $88.5$ – $89^{\circ}$ ; the latter was purified by conversion into its lead salt, and crystallises in small needles. The magnesium, silver, and copper salts were also prepared. The methyl ether crystallises in silky needles melting at  $71^{\circ}$ , and distills without decomposition at the ordinary pressure; the ethyl ether melts at  $69.5$ – $70^{\circ}$ , and decomposes on distillation.

The lower melting fractions when heated with soda-lime gave two acids, with formulæ ranging from  $C_{24}H_{48}O_2$  to  $C_{27}H_{54}O_2$ . In opposition to Brodie, the author considers the formula of the highest melting alcohol in beeswax to be  $C_{31}H_{64}O$ , instead of  $C_{30}H_{62}O$ .

J. K. C.

**Reactions of Saccharin.** By P. HERRMANN and B. TOLLENS (*Ber.*, 18, 1333–1336).—Saccharin does not yield any lævulinic acid when digested with hydrochloric acid for 20 hours at  $100^{\circ}$ . Kiliani has suggested (*Ber.*, 15, 2957, Abstr., 1883, 963) that saccharin contains a methyl-group, and is a lactone of saccharic acid, this latter being regarded as a substituted lactic acid of the formula  $HO \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot CMe(OH) \cdot COOH$ . The author confirms this hypothesis by showing that saccharin yields iodoform when treated with potassium iodide and aqueous soda, and potassium lactate when fused with potash.

A. P.

**Separation of Raffinose from the Molasses of Beetroot Sugar.** By C. SCHEIBLER (*Ber.*, 18, 1409–1413).—An aqueous solution of the crystalline products obtained by Steffen's process from molasses, was warmed with strontium hydroxide (1 mol. to 1 mol. sugar), the solution was cooled, when about 75 per cent. of the sugar separated out, and filtered. The solution was boiled with an excess of strontium hydroxide, and the mixed precipitate, containing raffinose and cane-sugar, collected and washed with a 10 per cent. boiling strontium solution; the mixed saccharate was then decomposed with carbonic anhydride, and the product treated twice as above described. Ultimately a syrup was obtained consisting chiefly of raffinose, and this was purified by means of alcohol. The author

intends investigating its properties. Its probable identity with sugars obtained by Loiseau and by Ritthausen was shown by Tollens (this vol., p. 368).  
N. H. J. M.

**Formation of Amines from the Amides of the Fatty Series.** By R. SEIFERT (*Ber.*, **18**, 1355—1357).—Ethylaniline is obtained by heating acetanilide with sodium ethoxide in a sealed tube for 36 hours, at 170—200°; water must not be present.

Ethylamine may be obtained by treating acetamide in a similar manner, a quantity of ammonia is, however, formed at the same time.  
A. P.

**Reduction of Nitrodimethylamine.** By A. P. N. FRANCHIMONT (*Chem. Centr.*, 1885, 381—382).—A saturated aqueous solution of the amine was treated with acetic acid and zinc-dust in small portions at a time. When the reaction was over, the whole was filtered and distilled with soda in excess: the distillate was found to contain unsymmetrical dimethylhydrazine. The formula of nitro-dimethylamine is therefore  $\text{Me}_2\text{N}\cdot\text{NO}_2$ .  
J. K. C.

**Constitution of the Additive Compound of Propionitrile and Hydrogen Chloride.** By A. MICHAEL and J. F. WING (*Amer. Chem. J.*, **7**, 71—74).—When this additive compound is treated with aniline, a basic substance,  $\text{C}_9\text{H}_{12}\text{N}_2$ , is obtained, regarded by the authors as a *propenylphenylamidine*,  $\text{NH}:\text{C}:\text{NHPh}$ . It crystallises in rhombohedrons, melts at 68°, is insoluble in water, soluble in alcohol and ether, and has basic properties. When boiled with water, it is decomposed into ammonia and propionanilide. The platinochloride,  $(\text{C}_9\text{H}_{12}\text{N}_2)_2\cdot\text{H}_2\text{PtCl}_6$ , crystallises in yellow prisms. A basic substance is also obtained by the action of sodium phenyloxide on the additive compound. The authors conclude from these results that propionitrile hydrochloride has the constitution  $\text{CEtCl}:\text{NH}$ .  
A. J. G.

**Diisobutylketine.** By E. LANG (*Ber.*, **18**, 1364—1365).—*Diisobutylketine*,  $\text{C}_{14}\text{H}_{24}\text{N}_2$ , is obtained by reducing isonitrosobutylketone (*Abstr.*, 1883, 572) with tin and hydrochloric acid; it forms a clear yellow oil, boils without decomposition between 242° and 244°, and is precipitated from its acetic acid solution by bromine, as an orange-coloured powder. The *platinochloride*,  $\text{C}_{14}\text{H}_{24}\text{N}_2\cdot\text{H}_2\text{PtCl}_6$ , forms magnificent orange needles.  
A. P.

**Propionic Acid and some of its Derivatives.** By C. A. LOBBY DE BRUYN (*Chem. Centr.*, 1885, 356—357).—*Propionic acid* melts at -23°, and boils at 141° under 756 mm. pressure; its vapour-density only becomes normal at about 260°. *Propionyl bromide* boils at 103—104°: its ethereal solution when treated with silver cyanide in small portions at a time, yields *dipropionyl dicyanide* in fine crystals; this melts at 59°, and boils at 210—212°; the author concludes that it is not identical with the cyanide obtained by Claisen and Moritz.  
J. K. C.

**Conversion of Lactonic Acids into Lactones.** Action of Sodium Ethylate on Isocapro lactone. By H. ERDMANN (*Annalen*,



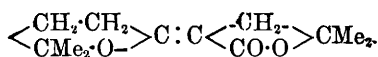
228, 176—198) — Boiling with dilute sulphuric acid converts phenylparaconic acid into phenylbutyrolactone, and similar treatment converts terebic acid into the isocaprolactone described by Breddt (*Annalen*, 208, 55).

A mixture of pseudopyroterebic acid and isocaprolactoid is formed by boiling an alcoholic solution of sodium ethoxide with isocaprolactone. The crude product is dissolved in water, acidified with dilute sulphuric acid, then boiled for a few minutes, and afterwards extracted with ether. To separate the acid from the isocaprolactoid, the ethereal solution is shaken with sodium carbonate. The crude acid is purified by distillation in steam, and conversion into the calcium salt,  $\text{Ca}(\text{C}_6\text{H}_9\text{O}_2)_2 + 3\text{H}_2\text{O}$ . Both the calcium and silver salts of pseudopyroterebic acid are more soluble in water than the corresponding pyroterebates.

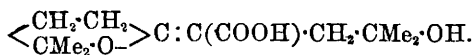
Pseudopyroterebic acid is a colourless liquid, lighter than water. It boils at  $202^\circ$ , with partial conversion into the lactone. Bromine readily unites with the acid to form a non-crystallisable oily liquid.

*Isocaprolactoid*,  $\text{C}_{12}\text{H}_{18}\text{O}_3$ , forms monoclinic crystals,  $\beta = 86^\circ 23'$ ;  $a : b : c = 1.0704 : 1 : 0.9735$ . It is soluble in the usual solvents with the exception of cold water. On decomposition with baryta-water, isocaprolactoid yields a hydroxy-acid,  $\text{HO} \cdot \text{C}_{11}\text{H}_{18}\text{O} \cdot \text{COOH} + \frac{1}{2}\text{H}_2\text{O}$ , which melts at  $79^\circ$ . The acid forms a soluble barium salt which crystallises in needles, and a sparingly soluble silver salt. On boiling with water the acid is converted into isocaprolactoid, and a neutral substance possessing an odour of peppermint.

The constitution of isocaprolactoid and the hydroxy-acid may be represented by the formulæ—



Isocaprolactoid.



Hydroxy-acid.

W. C. W.

**Decomposition of Organic Acids under the Influence of Light.** By H. DE VRIES (*Chem. Centr.*, 1885, 219).—The author has exposed solutions of oxalic, malic, citric, and tartaric acids to the light, and finds that they are gradually decomposed if free access of air be allowed. The neutral salts of these acids become alkaline under like circumstances. Ferric salts are reduced to ferrous, the iron acting as a carrier in conveying the oxygen to the organic acids. A small quantity of iron is sufficient to oxidise large quantities of these acids, and on keeping the oxidised solutions in the dark the iron soon reassumes the ferric state.

J. K. C.

**Action of Nitric Acid on certain Dibasic Acids.** By A. P. N. FRANCHIMONT (*Chem. Centr.*, 1885, 380—381).—Continuing his

researches on the homologues of oxalic acid, the author found that malonic acid lost both its carboxyl-groups on treatment with nitric acid, yielding dinitromethane instead of nitro-acetic acid, as stated by Kolbe. No mononitromethane is formed by this reaction. Succinic acid dissolves in concentrated nitric acid without decomposition, whereas isosuccinic acid evolves carbonic anhydride at once: when the latter was prepared from malonic acid, only one molecular proportion of carbonic anhydride was evolved; whilst that prepared from  $\alpha$ -propionic acid yielded a little more, but never two molecular proportions. Fumaric, maleic, citraconic, and itaconic acids do not yield carbonic anhydride when dissolved at the ordinary temperature in nitric acid.

J. K. C.

**Chelidonic Acid.** By L. HAITINGER and A. LIEBEN (*Monatsh. Chem.*, **6**, 279—328) — (Compare this vol., p. 47; also *Abstr.*, 1883, 870; 1884, 1196; this vol., p. 811).—*Comanic acid* from *chelidonic acid*.—The resolution by heat of chelidonic acid into pyrocomane and carbonic anhydride has already been mentioned (*Ost*, this vol., p. 49); if this decomposition is effected in a vacuum at 220—230°, then the comanic acid, described by *Ost*, is obtained as well. By heating *monoethyl chelidonate* at 225° it is decomposed into carbonic anhydride and *ethyl comanate*, melting at 102°, and identical with that described by *Ost* (*loc. cit.*). This compound when heated with lime-water is decomposed into calcium formate, calcium oxalate, acetone, and ethyl alcohol. Pyrocomane is regarded as forming the nucleus of chelidonic and comanic acids, and is represented as having the constitution  $\text{CO} < \begin{smallmatrix} \text{CH} : \text{CH} \\ \text{CH} : \text{CH} \end{smallmatrix} > \text{O}$ . The first of these acids is a dicarboxyl-derivative of this nucleus, the second a monocarboxyl-derivative.

*Diethyl chelidonate* crystallises in the triclinic system;  $a : b : c = 1.5794 : 1 : 0.5033$ ; observed faces,  $\infty P \infty$ ,  $\infty P \infty$ ,  $0P$ ,  $2'P' \infty$ ,  $P \infty$ ;  $\infty P'$ ,  $0P'$ .

*Ammonchelidonic acid* (*Abstr.*, 1883, 871) is prepared by decomposing calcium chelidonate with ammonium carbonate, boiling the solution with ammonia, and precipitating with hydrochloric acid. It is a white powder, insoluble in cold water, sparingly soluble in hot water, and soluble in alkalis, forming colourless solutions. It yields a yellow coloration with ferrous salts, a reddish-yellow with ferric salts, and a gelatinous precipitate with silver nitrate. It is a feeble base; when heated with concentrated hydrochloric acid in sealed tubes it forms a hydrochloride,  $\text{C}_7\text{H}_5\text{NO}_5 \cdot \text{HCl} + \text{H}_2\text{O}$ , which is decomposed by water. Ammonchelidonic acid is resolved by heat into carbonic anhydride and oxypyridine (*loc. cit.*).

*Dibromammonchelidonic acid*,  $\text{C}_7\text{H}_3\text{Br}_2\text{NO}_5 + 2\text{H}_2\text{O}$ , is formed by the action of bromine on ammonchelidonic acid suspended in water; it crystallises from hot water in needles, and is decomposed by heat into dibromoxypyridine (*loc. cit.*) and carbonic anhydride.

*Methylammonchelidonic acid*,  $\text{C}_8\text{H}_7\text{NO}_5$ , is prepared by heating together methylamine and chelidonic acid in sealed tubes at 100°; it crystallises from water in shining granules, and gives an intense yellow coloration with ferric chloride (*Abstr.*, 1884, 1196). Heated at 180° it is

decomposed into *methyloxy*pyridine,  $C_5H_7NO$ , and carbonic anhydride. It is not decomposed by hydrochloric acid but forms a hydrochloride, and is converted by bromine into a *dibromomethylammonchelidonic acid*, which is resolved by heat into *dibromomethyloxy*pyridine,  $C_5NH_2MeBr_2O$ , melting at  $196^\circ$ . Aniline and chelidonic acid yield a phenylammonchelidonic acid (*loc. cit.*) crystallising in silky needles, which when heated yields a *phenyloxy*pyridine.

Dimethylamine decomposes chelidonic acid with formation of oxalic acid and acetone.

*Oxypyridine* or *pyridon*.—This compound may be prepared as above described, or by distilling ammonchelidonic acid at  $230$ – $240^\circ$  in a vacuum. It crystallises from water in crystals containing 1 mol.  $H_2O$ , melting at  $66$ – $67^\circ$ ; the dehydrated crystals melt at  $148.5^\circ$ , and boil at  $350^\circ$ . It is easily soluble in water, sparingly soluble in ether, benzene, and chloroform. The crystals belong to the monosymmetric system,  $a : b : c = 0.548 : 1 : 1.496$ .  $\beta = 85^\circ 37'$ ;  $\infty P \infty$ ,  $P \infty$ ,  $P \infty$ ,  $\infty P$ ,  $\infty P_2$ ,  $P$ . Its *platinochloride* is soluble in water, and forms granular crystals, having the composition  $(C_5H_5NO)_2, H_2PtCl_6 + 2H_2O$ . It crystallises in the monoclinic system,  $a : b : c = 1.3561 : 1 : 0.9485$ .  $\infty P \infty$ ,  $\infty P \infty$ ,  $P \infty$ ,  $\infty P$ ,  $2P_2$ . Like pyridine *platinochloride*, it is decomposed by boiling with water, forming a light-yellow sparingly soluble compound, having the composition  $(C_5H_5NO)_2PtCl_4 + (C_5H_5NO)_2, H_2PtCl_6 + H_2O$ . Oxypyridine is converted into *methyloxy*pyridine by the direct action of methyl iodide, showing that the methyl-group does not replace an atom of hydrogen in a hydroxyl-group, but one combined with nitrogen. The absence of a hydroxyl-group in oxypyridine is demonstrated by its inability to form acetic derivatives when heated with either acetic chloride or anhydride. *Methyloxy*pyridine forms a radiated crystalline, deliquescent mass, melting at about  $89^\circ$ . With bromine it forms the dibromo-derivatives already mentioned, melting at  $196^\circ$ . Its *platinochloride*,  $(C_5H_7NO)_2, H_2PtCl_6 + H_2O$ , forms large triclinic crystals; axial ratio  $a : b : c = 1.2589 : 1 : 0.9294$ .

*Methyloxy*pyridinemethylum chloride is formed by acting on the product of the action of methyl iodide on pyridine with silver chloride. Its *platinochloride*,  $(C_5H_4MeNO, MeCl)_2PtCl_4$ , is sparingly soluble in water, and crystallises in red monoclinic crystals;  $a : b : c = 0.6997 : 1 : 0.4203$ . Silver oxide and caustic alkalis resolve the methylum chloride into *methyloxy*pyridine and methyl alcohol.

*Chloropyridine*,  $C_5NH_4Cl$ , is formed by the action of phosphorus pentachloride on oxypyridine; it is a liquid, boiling at  $147$ – $148^\circ$ , is soluble in water, its *platinochloride* forms a reddish-yellow crystalline precipitate. By the action of hydriodic acid it is converted into *iodo*pyridine, and by sodium methoxide into a *methoxy*pyridine isomeric with methyl oxypyridine, which boils at  $190.5$ – $191^\circ$ , is miscible with water, has an odour like that of pyridine, and possesses an alkaline reaction.

P. P. B.

**Formation of Methyl Racemate from Methyl Dextro- and Lævo-tartrates: Vapour-density of Ethyl Racemate.** By R. ANSCHÜTZ (*Ber.*, 18, 1397–1400).—*Dimethyl lavotartrate* resembles

dimethyl dextrotartrate, except in its optical properties; it melts at  $48^{\circ}$  and boils at  $160^{\circ}$  under about 16 mm. pressure. When warmed with dimethyl dextrotartrate, or when mixed with it in solution in methyl alcohol, it yields methyl racemate.

A vapour-density estimation of ethyl racemate pointed to the simple formula  $C_8H_{14}O_6$ , a result not unexpected, as methyl racemate, dextro- and lævo-tartrate, ethyl racemate, and ethyl dextrotartrate all have almost the same boiling point at both ordinary and reduced pressures. It is probable that racemic acid is a combination of dextro- and lævo-tartaric acids, and that the ethyl salt dissociates into its two constituents at the temperature at which the vapour-density estimation was made, recombination occurring on cooling. This would confirm the hypothesis of Kekule and Anschütz (*Ber.*, **14**, 717) that fumaric acid consists of dextro- and lævo-maleic acids (although the vapour-density of ethyl fumarate agrees with the simpler formula) as fumaric acid is converted by oxidation into racemic acid.

N. H. J. M.

**Trihydroxyadipic Acid.** By H. KILIANI (*Ber.*, **18**, 1555—1558).—Trihydroxyadipic acid,  $C_6H_5(OH)_3(COOH)_2$ , crystallises in monoclinic plates,  $a : b : c = 0.5046 : 1 : 0.9352$ .  $\beta = 83^{\circ} 33'$ . It melts at  $146^{\circ}$ , with loss of water, and, probably, formation of a lactone. The calcium, zinc, copper, silver, and lead salts are described (*comp. this vol.*, p. 745).

A. J. G.

**Galactonic Acid.** By H. KILIANI (*Ber.*, **18**, 1551—1555).—By the oxidation of an aqueous solution of milk-sugar with bromine Barth and Hlasiwetz obtained a monobasic acid to which they assigned the formula  $C_6H_{10}O_6$ , and termed lactonic acid (*Annalen*, **119**, 281; **122**, 96; **155**, 136); as this name is now applied generally to a series of acids to which this one does not belong, the author substitutes the name galactonic acid. Barth and Hlasiwetz appear to have mistaken the lactone for the acid.

*Galactonic acid*,  $C_6H_{12}O_7$ , is best prepared by the action of bromine on an aqueous solution of lactose in manner similar to that described for gluconic acid (*Abstr.*, 1884, 994), its formation being represented by the equation  $C_6H_{12}O_6 + H_2O + Br_2 = C_6H_{12}O_7 + 2HBr$ . When milk-sugar is used without previous inversion the yield is very small. It crystallises in small needles. When heated at  $95$ — $100^{\circ}$  for four hours it loses 1 mol.  $H_2O$ , and is converted into the lactone  $C_6H_{10}O_5$ ; this forms a pale yellow syrup, which on cooling, solidifies to an amorphous, gummy mass destitute of acid properties. The following formulæ replace those assigned by Barth and Hlasiwetz (*loc. cit.*); ammonium salt,  $C_6H_{11}O_7NH_4$ ; sodium salt,  $C_6H_{11}O_7Na + 2H_2O$ ; calcium salt,  $(C_6H_{11}O_7)_2Ca + 5H_2O$ ; and cadmium salt,  $(C_6H_{11}O_7)_2Cd + H_2O$ .

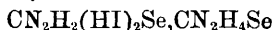
A. J. G.

**Simultaneous Action of Oxygen and Hydracids on Seleniocarbamide.** By A. VERNEUIL (*Compt. rend.*, **100**, 1296—1298).—When oxytriseleniocarbamide (*this vol.*, p. 376) is allowed to remain in the acid liquid in which it is formed, it is completely converted by the continued action of the hydracid and the oxygen of the air into a

yellow crystalline compound, of the composition  $C_2N_4H_8Se_2Cl_2$ . This compound dissolves in water and is completely decomposed by alkalis and by barium or calcium carbonate, half the selenium being precipitated, whilst the solution contains cyanamide and seleniocarbamide in the proportions indicated by the equation  $C_2N_4H_8Se_2Cl_2 + BaH_2O_2 = Se + CN_2H_2 + CN_2H_4Se + 2H_2O + BaCl_2$ . The new compound may be regarded as formed by the union of 1 mol. dihydrochloroseleniocarbamide,  $CN_2H_2(HCl)_2Se$ , with 1 mol. seleniocarbamide.

The oxytriseleniocarbamide previously described (*loc. cit.*) is formed by the union of the preceding compound with 1 mol. of seleniocarbamide, or of 1 mol. of dehydrochloroseleniocarbamide, with 2 mols. of seleniocarbamide. It can, indeed, be obtained by mixing saturated solutions of the new compound and seleniocarbamide in proper proportions and cooling the mixture. The oxygen in oxytriseleniocarbamide is present in the state of water.

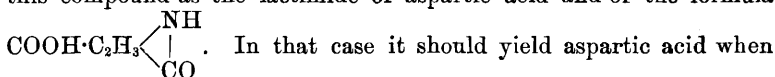
Hydrobromic acid acts in the same way as hydrochloric acid, but hydriodic acid yields no intermediate compound corresponding with oxytriseleniocarbamide hydrochloride, the substance



being formed at once. Chlorine, bromine, and iodine produce the same compounds as their hydracids.

C. H. B.

**Action of Methyl Iodide on Asparagine.** By A. MICHAEL and J. F. WING (*Amer. Chem. J.*, **6**, 419—422).—The authors have investigated the acid  $C_4H_5NO_3$  obtained by Griess (*Abstr.*, 1880, 315) by the action of methyl iodide on asparagine. Griess looked on this compound as the lactimide of aspartic acid and of the formula



heated with strong hydrochloric acid. When boiled with even dilute acid or with alkali, it yields fumaric, and not aspartic acid.

Aspartic acid was also dissolved in potash, methyl alcohol added, and then methyl iodide as long as a reaction took place. The solution was heated to expel the methyl alcohol and acid added. Fumaric acid only was formed. The authors therefore consider this compound to be the acid amide of fumaric acid, and to be formed according to the equation  $COOH \cdot C_2H_3(NH_2) \cdot CO \cdot NH_2 + 4MeI = COOH \cdot C_2H_2 \cdot CO \cdot NH_2 + NMe_4I + 3HI$ . When a glacial acetic acid solution was treated with bromine at the ordinary temperature, an additive compound,  $COOH \cdot C_2H_2Br_2 \cdot CONH_2$ , was formed, which, when heated with strong hydrochloric acid, yielded  $\beta$ -dibromosuccinic acid. This proves the compound to be an amide of fumaric acid, and not of maleic acid.

No similar reaction takes place when ethyl iodide is substituted for methyl iodide in the above reaction. The authors state that the acid amide melts at  $217^\circ$  with decomposition.

L. T. T.

**Action of Ethyl Chlorocarbonate on Potassium Cyanate.** By WURTZ and HENNINGER (*Compt. rend.*, **100**, 1419—1426).—When 25 parts of finely-powdered potassium cyanate and 33 parts of ethyl

ethylchlorocarbonate are heated together at  $60^\circ$  for 24 hours and the temperature then raised and kept at  $100^\circ$  for four days, the main product is *ethyl cyanurocarboxylate*,  $C_{12}H_{15}N_3O_9$  or  $3(NCO\cdot COOEt)$ , which forms large colourless rhombic plates melting at  $118\text{--}119^\circ$ , only slightly soluble in water and cold alcohol, but very soluble in ether and boiling alcohol, and still more soluble in chloroform. When distilled or heated with water at  $100^\circ$ , it loses carbonic anhydride and forms ethyl cyanurate.

If the potassium cyanate and ethyl chlorocarbonate are heated in presence of anhydrous ether, the same product is obtained, together with a small quantity of a compound of the composition  $C_{10}H_{15}N_3O_5$ , which crystallises in confused needles melting at  $107^\circ$ . This compound is derived from cyanuric acid by the replacement of  $H_2$  by  $Et_2$ , and of the third atom of hydrogen by  $COOEt$ . When distilled, it yields carbonic anhydride and ethyl cyanurate. When the reaction takes place in presence of aqueous ether, the compound  $C_{10}H_{15}N_3O_5$  is formed together with ethylic carboxylcarbamate,  $NH(COOEt)_2$ . In one preparation, when the operation was continued for five days, another compound,  $C_{11}H_{15}N_3O_7$ , was obtained. It crystallises in plates, melts at  $123^\circ$ , and when distilled splits up into carbonic anhydride and ethyl cyanurate. It is a derivative of cyanuric acid, one of the atoms of hydrogen having been replaced by ethyl, and the other 2 atoms by two  $COOEt$ -groups.

When ethyl chlorocarbonate and potassium cyanate are heated together in sealed tubes at  $200^\circ$ , the sole product of the reaction is ethyl cyanurate,  $3(CONEt)$ .

The three compounds described above form with ethyl cyanurate a complete series differing from one another by  $nCO_2$ , and the existence of these compounds is a further proof in favour of the generally accepted formula for cyanuric acid.

*Ethylic carboxylcarbamate*,  $NH(COOEt)_2$ , crystallises in long prisms, which resemble those of nitre or urea and melt at  $49\text{--}50^\circ$ . It boils at  $226^\circ$  without decomposition under a pressure of 760 mm., and at  $144\text{--}145^\circ$  under a pressure of 20 mm. It is formed by the action of the alcohol contained in the ether on the ethyl carboxycyanate, and indeed is the sole product obtained when ethyl chlorocarbonate and potassium cyanate are heated with absolute alcohol. It is also formed when ethyl carbamate is heated with ethyl chlorocarbonate at  $115\text{--}120^\circ$  in sealed tubes for several hours. When treated with aqueous ammonia at  $100^\circ$ , it yields biuret melting at  $190^\circ$ . It behaves as an imide, and yields a silver salt,  $C_6H_{10}NO_4Ag$ , which crystallises in cubes and blackens slowly at  $100^\circ$ .

C. H. B.

**Action of Nitric Acid on Dimethylsulphonamides.** By A. P. N. FRANCHIMONT (*Chem. Centr.*, 1885, 384).—*Symmetrical dimethylsulphonamide* is formed when an ethereal solution of sulphuryl chloride is added to a well-cooled ethereal solution of methylamine. After distilling off the ether, the residue is dissolved in water and shaken up with ether, which dissolves out the amide; it is very soluble in water and alcohol, slightly so in benzene and chloroform, insoluble in light petroleum, and melts at  $78^\circ$ . It forms crys-

talline compounds with acids. Dissolved in a large excess of concentrated nitric acid and treated with water, a white precipitate is thrown down, which crystallises from benzene in hard crystals melting at  $90^{\circ}$ , and consists of symmetrical *dinitro-dimethylsulphonamide*. It detonates at  $160^{\circ}$ .

Tetramethylsulphonamide, when dissolved in nitric acid, yields nitrodimethylamine.  
J. K. C.

**New Sulphonic Acids.** By A. MONARI (*Ber.*, **18**, 1343—1350).

—*Propylenedisulphonic acid*,  $\text{SO}_3\text{H}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ , already prepared by Hofmann and Buckton (this Journal, 1856, 241; see also *Annalen*, **140**, 83), forms a thick syrup, is difficult to crystallise, is readily soluble in water or alcohol, and is decomposed by heat, sulphurous anhydride being given off; its salts are very soluble and are difficult to crystallise. The barium and sodium salts are described.

*Trimethylenedisulphonic acid*,  $\text{SO}_3\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ , is prepared from trimethylene dibromide and ammonium sulphite. It forms a thick syrup, readily soluble in water and spirit; by carefully drying it may be obtained in an amber-coloured mass of long thin prismatic needles; when gently heated it melts with decomposition. The *barium salt*,  $\text{C}_3\text{H}_6(\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ , and *sodium salt*,  $\text{C}_3\text{H}_6(\text{SO}_3\text{Na})_2 + 4\frac{1}{2}\text{H}_2\text{O}$ , are described.

*Ethenyltrisulphonic acid*,  $\text{SO}_3\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{SO}_3\text{H})_2$ , obtained from either monobromomethylene bromide or the corresponding chlorine compound, and ammonium sulphite, forms an almost colourless syrupy liquid, which becomes brown on exposure to light. By drying over sulphuric acid, it may be obtained in a crystalline mass of large hexagonal tablets; it melts at  $110^{\circ}$ , giving off small quantities of sulphurous anhydride at the same time. The *barium salt* (with  $5\frac{1}{2}$  mol.  $\text{H}_2\text{O}$ ), the *sodium salt*,  $\text{C}_2\text{H}_3(\text{SO}_3\text{Na})_3 + 4\text{H}_2\text{O}$ , and the *ammonium salt*,  $\text{C}_2\text{H}_3(\text{SO}_3\text{Am})_3$ , are described.

*Barium hydroxyethylenedisulphonate*,  $\text{HO}\cdot\text{C}_2\text{H}_3(\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ , is obtained by acting on monochlorethylenedichloride with an excess of ammonium sulphite for a considerable time, and treating the resulting ammonium salt with barium hydroxide. It is exceedingly soluble in water, from which it may be precipitated in minute needles by the addition of alcohol; it is unaltered by the air and is not hygroscopic. The *ammonium salt*,  $\text{HO}\cdot\text{C}_2\text{H}_3(\text{SO}_3\text{Am})_2 + \frac{1}{2}\text{H}_2\text{O}$ , and *sodium salt*,  $\text{HO}\cdot\text{C}_2\text{H}_3(\text{SO}_3\text{Na})_2 + 3\frac{1}{2}\text{H}_2\text{O}$ , were also prepared; the free acid was not obtained.

*Ammonium methylenedisulphonate*,  $\text{CH}_2(\text{SO}_3\text{Am})_2$ , is obtained by acting on ammonium ethenyltrisulphonate with a further quantity of ammonium sulphite,  $\text{C}_2\text{H}_3(\text{SO}_3\text{Am})_3 + \text{Am}_2\text{SO}_3 = \text{NH}_3 + 2\text{CH}_2(\text{SO}_3\text{Am})_2$ ; the sodium and barium salts were also prepared.

*Ethylenedisulphonic acid*,  $\text{C}_2\text{H}_4(\text{SO}_3\text{H})_2$ , is formed by the action of excess of ammonium sulphite upon monobromomethylene dibromide. The *barium salt* may be obtained by treating the mother-liquors from the preparation of ammonium ethenyltrisulphonate with an alcoholic solution of barium acetate. The *ammonium salt* was also prepared; the reaction probably takes place according to the equation  $\text{C}_2\text{H}_3\text{Br}_3 + 3\text{Am}_2\text{SO}_3 + \text{H}_2\text{O} = \text{Am}_2\text{SO}_4 + \text{HBr} + 2\text{AmBr} + \text{C}_2\text{H}_4(\text{SO}_3\text{Am})_2$ .

A. P.

**Nitro-derivatives of Furfurane.** By B. PRIEBES (*Ber.*, **18**, 1362—1363).—*Nitroethenyl furfurane*,  $C_4H_3O \cdot C_2H_2 \cdot NO_2$ , may be readily obtained by acting on furfuraldehyde in an alkaline solution with nitromethane. It crystallises from light petroleum in long lustrous yellow prisms, melts at  $74-75^\circ$ , distils readily with steam, has a sharp taste and odour, and acts on the skin. By treating this compound with nitric acid, *nitroethenyl nitrofurfurane*,  $NO_2 \cdot C_4H_2O \cdot C_2H_2 \cdot NO_2$ , is formed. It crystallises from alcohol in yellow felted needles, becomes brown and melts at  $143-144^\circ$ , is a very stable compound, and on treatment with bromine, forms a dibromide crystallising in yellow prisms, and melting at  $110-111^\circ$ . When oxidised with chromic mixture, it yields *nitropyromucic acid*,  $NO_2 \cdot C_4H_2O \cdot COOH$ , which crystallises from water in glittering yellowish tablets or prisms, melts at  $184^\circ$ , and may be sublimed unaltered by careful heating; it yields an insoluble silver salt which explodes on heating. A. P.

**Physical Properties of Thiophen.** By R. SCHIFF (*Ber.*, **18**, 1601—1605).—Thiophen boils at  $83.9-84.2^\circ$  (corr.) under 755.7 mm. pressure. Density determinations at various temperatures gave the following results (water at  $4^\circ = 1$ ):—

Temp.	$0^\circ$ .	$15.4^\circ$ .	$34.1^\circ$ .	$56.2^\circ$ .	$60.1^\circ$ .
Sp. gr. . .	1.08844	1.07047	1.04843	1.02165	1.01668
Volume. .	1.00000	1.01678	1.03816	1.06537	1.07058

Temp.	$72.5^\circ$ .	$79.3^\circ$ .	$84^\circ$ .
Sp. gr. ....	1.00158	0.99266	0.98741
Volume ...	1.08672	1.09648	1.10231

The expansion coefficient at  $t^\circ$  will therefore be expressed by

$$\frac{dV}{dt} = 0.001057539 + 0.00000350026t + 0.000000082323t^2.$$

The results of the determination of the capillary constants, by the author's methods (*Abstr.*, 1884, 808, this vol., p. 717), can be expressed by the general equation  $\alpha^2 = 6.783 - 0.0224t$ .

The absolute critical temperature =  $576^\circ$ . The molecular volume at the boiling point =  $84.93$ . A. J. G.

**Direct Preparation of Dibromothiophen from Coal-tar Benzene.** By V. MEYER and O. STADLER (*Ber.*, **18**, 1488—1490).—On agitating 500 grams of the so-called purest coal-tar benzene with 30 grams of bromine, the solution becomes nearly decolorised, whilst hydrobromic acid is abundantly evolved; the product is washed with water and soda solution, and the benzene removed by distillation on a water-bath. The residual dark-coloured oil is heated with alcoholic potash, to decompose the additive compounds which are present, and then distilled in a current of steam, when a yellowish oil is obtained, which on distillation yields nearly pure dibromothiophen. The yield amounted to 13 grams from the 500 grams benzene.

In another experiment conducted on a large scale the yield amounted



to 1400 grams pure dibromothiophen, boiling at 203—207° from 200 kilos. benzene; some monobromothiophen, boiling at 149—151°, was also obtained.

A. K. M.

**Reduction of Nitrothiophen to Amidothiophen.** By O. STADLER (*Ber.*, 18, 1490—1492).—1 gram nitrothiophen is dissolved in about 50 c.c. of saturated alcoholic hydrochloric acid, and 2 grams of granulated tin are gradually added. The reduction takes place spontaneously, and after a time the stannochloride,  $(C_4SH_3 \cdot NH_2)_2 \cdot H_2SnCl_6$ , crystallises out; this forms small white lustrous crystals, insoluble in ether, moderately soluble in water and alcohol. The free base may be separated as a bright yellow oil, which, however, soon becomes resinised.

A. K. M.

**Identity of the Two Ortho-positions in the Benzene Nucleus.** By C. A. LOBRY DE BRUYN (*Chem. Centr.*, 1885, 357).—The author has examined the crystalline forms of the substances obtained by the action of potassium methoxide on ethoxynitrobenzonitrile and of potassium ethoxide on methoxynitrobenzonitrile respectively, and finds them to be identical in every way, showing that the ethyl and methyl groups occupy symmetrical positions with respect to the cyanogen-group.

J. K. C.

**Formation of Normal Propylbenzene.** By WISPEK and ZUBER (*Bull. Soc. Chim.*, 43, 588).—A claim of priority.

**Formation of Normal Propylbenzene.** By R. D. SILVA (*Bull. Soc. Chim.*, 43, 588—591).—A reply to the preceding note.

**Chloro-derivatives of Ortho-xylene.** By A. CLAUS and H. KAUTZ (*Ber.*, 18, 1367—1371).—On passing a stream of dry chlorine through pure well-cooled ortho-xylene to which 10 per cent. of iodine has been added, a crystalline mass is obtained, consisting of mono-, di-, tri-, and tetra-chloro-xylene which may be separated by distillation with steam.

*Monochlorortho-xylene*,  $C_6H_3ClMe_2$ , is an odourless, colourless refractive oil, boiling at 205° (uncorr.); its sp. gr. = 1.0863 at 19°; it does not solidify, even when cooled with a mixture of ice and salt; by oxidation with dilute nitric acid it is converted into a monochlorophthalic acid, which is, however, obtained in too small a quantity to permit of satisfactory examination.

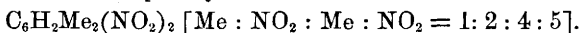
*Dichlorortho-xylene*,  $C_6H_2Cl_2Me_2$ , is an oil similar to the mono-derivative, but solidifies to a crystalline mass at 0°; it melts at 3°, and boils at 227°; when heated at 200° in a sealed tube with nitric acid of 1.15 sp. gr., it yields the known dichlorophthalic acid, melting at 183°.

*Trichlorortho-xylene*,  $C_6HCl_3Me_2$ , crystallises from ether in long colourless shining needles; melts at 93° (uncorr.), and boils at 265° (uncorr.), without decomposition; on slowly heating, it sublimes in needles; it is soluble in the usual solvents. It yields trichlorophthalic acid, melting at 157° when oxidised.

*Tetrachlorortho-xylene*,  $C_6Cl_4Me_2$ , forms long colourless needles; melts at 215° (uncorr.), and sublimes unaltered; unlike the lower

chloro-derivatives, it cannot be distilled in a current of steam. It is not oxidised when digested at 200° in a sealed tube with nitric acid, but on treatment with chromic mixture it is oxidised into carbonic anhydride. The authors remark upon the fact that the methyl-groups in ortho-xylene become readily oxidisable by dilute nitric acid on the introduction of chlorine into the benzene nucleus. A. P.

**Constitution of the Dinitroparaxylenes.** By E. LELLMAN (*Annalen*, **228**, 250—253).—In preparing  $\alpha$ - and  $\beta$ -dinitroparaxylene, by slowly adding paraxylene to fuming nitric acid (sp. gr. 1.51) at the ordinary temperature, the author succeeded in isolating the third isomeric dinitroparaxylene,



This compound forms long yellow needles, soluble in warm alcohol and warm ether. It melts at 147—148°. In order to ascertain the constitution of the three isomerides, they were reduced to the diamines, and then treated with ammonium thiocyanate (compare p. 976). In the dinitroparaxylene, melting at 93°, the nitro-groups are at [2 : 3], and in the isomeride melting at 124°, the positions of the nitro-groups are [2 : 6].

Ladenburg's mode (*Ber.*, **11**, 1649) of distinguishing between ortho-, meta-, and para-diamines does not yield satisfactory results when applied to the diamidoparaxylenes. W. C. W.

**Aromatic Silicon Compounds.** By A. POLIS (*Ber.*, **18**, 1540—1544).—*Silicon tetraphenyl*,  $\text{SiPh}_4$ , is prepared by adding sodium to a mixture of silicon tetrachloride and chlorobenzene, diluted with four times the volume of anhydrous ether, and mixed with a little ethyl acetate; the yield is nearly quantitative. It forms a crystalline powder, melts at 228°, distils at above 360°, and burns when heated in air. It is sparingly soluble in ether and alcohol, somewhat more readily in chloroform, acetic acid, and acetone, most readily in benzene. Fuming nitric acid converts it into a nitro-derivative still under investigation.

*Silicon tetraparatolyl*,  $\text{Si}(\text{C}_6\text{H}_4\text{Me})_4$ , is obtained by the action of sodium on a mixture of silicon chloride and parabromobenzene; it forms colourless transparent crystals, melts at 228°, boils without decomposition at above 360°, and is readily soluble in hot benzene, sparingly in chloroform and ether.

*Silicon tetrabenzyl*,  $\text{Si}(\text{CH}_2\text{Ph})_4$ , is obtained in manner similar to the other compounds, but its preparation is not so easy; dibenzyl and a chloride boiling at 160—180° are formed at the same time. It forms colourless crystals, melts at 127.5°, and is sparingly soluble in alcohol, readily in chloroform, benzene, and hot ether.

A. J. G.

**Preparation of Mononitrophenols from their Primary Amines.** By E. NÖLTING and E. WILD (*Ber.*, **18**, 1338—1340).—By treating a solution of aniline in sulphuric acid with sodium nitrite, and acting on the resulting diazo-compound with the theoretical quantity of nitric acid to form a mononitro-derivative, 22 per cent. of ortho-, and 16 per cent. of para-nitrophenol are obtained.

By treating paranitrotoluidine in a similar manner metanitroparacresol is formed; the yield is almost 75 per cent.

Orthotoluidine, when treated in the same way, gives metanitro-orthocresol; the yield is, however, not good.

*a*-Naphthylamine yields dinitronaphthol and orthonitronaphthol; the amount obtained is small.

On treating the sulphuric acid solutions of the diazo-compounds with potassium nitrate instead of free nitric acid, the phenol itself is formed, only traces of the mononitro-compound being obtained.

A. P.

**New Nitrotoluidine.** By E. LELLMANN and E. WÜRTNER (*Annalen*, **228**, 239—243).—The nitrotoluidine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$  [ $\text{Me} : \text{NH}_2 : \text{NO}_2 = 1 : 2 : 3$ ], is prepared by slowly adding acetotoluide to a well-cooled mixture of fuming nitric acid (3 parts) and glacial acetic acid (1 part). On the addition of water, the nitro-product is precipitated. In order to remove the acetyl-group, the alcoholic solution of the product of nitration is boiled for a few minutes with potash. It is then diluted with hot water, and left at rest for several hours. A mixture of needle-shaped and granular crystals is deposited, which may be separated mechanically. The needles melt at  $129.5^\circ$ , and consist of metanitroorthotoluidine [ $1 : 2 : 5$ ]. The granular crystals, melting at  $158^\circ$ , consist of an undecomposed nitracetotoluide, which is saponified by strong hydrochloric acid, yielding the  $1 : 2 : 3$  nitrotoluidine. This substance crystallises in orange-coloured prisms, freely soluble in alcohol, ether, benzene, chloroform, and glacial acetic acid. It melts at  $97^\circ$ .

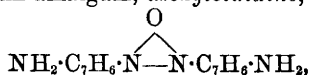
The constitution of the nitrotoluidine was ascertained by converting it into nitrotoluene and metanitrobenzoic acid, melting at  $141.5^\circ$ .

W. C. W.

**Nitrotoluidines.** By H. LIMPRICHT (*Ber.*, **18**, 1400—1406).—Dinitrotoluene of the constitution [ $\text{Me} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 4$ ], dissolved in warm alcoholic ammonia, is acted on by hydrogen sulphide with formation of two nitrotoluidines; that obtained by Beilstein and Kuhlberg (*Annalen*, **155**, 14), melting at  $77.5^\circ$ , and that obtained by Nölting and Collin (*Abstr.*, 1884, 1007), melting at  $107^\circ$ . In preparing dinitrotoluene, as described by Beilstein and Kuhlberg (*loc. cit.*), a second dinitrotoluene was found, which, when reduced, yielded a new nitrotoluidine of the constitution [ $\text{Me} : \text{NO}_2 : \text{NH}_2 = 1 : 2 : 5$ ]; it forms yellow or reddish-yellow needles melting at  $53^\circ$ , and is readily soluble in alcohol, sparingly in cold water. Its *hydrochloride* and *sulphate* are described. When warmed with acetic anhydride it yields *nitracetotoluide*,  $\text{NO}_2 \cdot \text{C}_7\text{H}_6 \cdot \text{NHAc}$ , crystallising in tufts of yellowish-white needles, melting at  $136^\circ$ , and sparingly soluble in hot water, readily in alcohol.

Nitrotoluidine [ $\text{Me} : \text{NO}_2 : \text{NH}_2 = 1 : 3 : 4$ ], yields, when reduced, toluylenediamine, melting at  $88.5^\circ$ .

When a cold concentrated solution of nitrotoluidine is treated very gradually with sodium amalgam, *azoxytoluidine*,



is obtained; it forms long silky yellow or yellowish-red needles, melting at  $168^{\circ}$ , sparingly soluble in water, readily in alcohol and ether; it yields crystalline salts. When warmed with sulphuric acid at  $100-110^{\circ}$ , a reaction takes place (analogous to the action of sulphuric acid on azoxybenzene) with formation of *hydroxyazotoluidine*,  $\text{NH}_2 \cdot \text{C}_7\text{H}_5(\text{OH}) \cdot \text{N}_2 \cdot \text{C}_7\text{H}_5 \cdot \text{NH}_2$ . The latter compound forms small dark red needles, sparingly soluble in water, readily in alcohol and ether, melting with decomposition at  $212^{\circ}$ . Its *sulphate* and *hydrochloride* were prepared. When reduced it yields *toluylenediamine*,



melting at  $99^{\circ}$ , and *cresoldiamine*,  $\text{HO} \cdot \text{C}_7\text{H}_5(\text{NH}_2)_2$ ; this latter could not be obtained in the free state; its *sulphate* forms white needles, which become blue on exposure to air, and is very readily soluble in alcohol and water, less soluble in ether.

When azoxytoluidine is further reduced, azotoluidine and hydrazotoluidine are formed. *Azotoluidine*,  $(\text{NH}_2 \cdot \text{C}_7\text{H}_5)_2\text{N}_2$ , separates from alcohol in long red needles, from water in small yellow needles, both melting at  $197^{\circ}$ ; it dissolves sparingly in water, readily in alcohol and ether. The *sulphate*, *hydrochloride*, and *hydrobromide* were prepared. *Hydrazotoluidine*,  $\text{NH}_2 \cdot \text{C}_7\text{H}_5 \cdot \text{NH} \cdot \text{NH} \cdot \text{C}_7\text{H}_5 \cdot \text{NH}_2$ , forms yellowish-white needles which, when moist, decompose on exposure to air, is readily soluble in water, almost insoluble in alcohol, and when heated burns without melting. It yields crystalline salts.

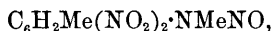
N. H. J. M.

**Derivatives of Metanitroparatoluidine.** By L. GATTERMANN (*Ber.*, 18, 1482—1488).—*Metanitroparethyltoluidine*,



is prepared by heating nitrotoluidine (10 grams) with ethyl iodide (12 grams) and alcohol for 6—8 hours at  $120-130^{\circ}$ ; it is extremely soluble in ether and benzene, readily in hot alcohol, and crystallises in large bright red crystals melting at  $58-59^{\circ}$ . On reduction it yields *metamidoparethyltoluidine*, which crystallises in large colourless plates melting at  $54-55^{\circ}$ ; when a crystal is thrown on the surface of water, it exhibits a remarkable rotatory motion, a property which appears to be common to diamines. By the action of nitric acid (sp. gr. 1.45) on the nitrethyltoluidine, *metadinitroparethyltoluidine*,  $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2 \cdot \text{NH} \cdot \text{Et}$ , is produced; it crystallises from alcohol in long orange-yellow needles, and from benzene in large prisms melting at  $126-126.5^{\circ}$ ; its conversion into ordinary dinitrobenzoic acid shows that it has the constitution  $[\text{Me} : \text{NO}_2 : \text{NH} \cdot \text{Et} : \text{NO}_2 = 1 : 3 : 4 : 5]$ . On passing nitrous acid into its alcoholic solution, *nitrosodinitrethyltoluidine*,  $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2 \cdot \text{N} \cdot \text{Et} \cdot \text{NO}$ , is produced; it is almost insoluble in cold alcohol, crystallises in nearly colourless dense prisms from hot alcohol, and in large rhombic crystals from benzene; it melts at  $77-78^{\circ}$ . *Trinitrethyltoluidine*, obtained by the action of nitric acid of sp. gr. 1.52 on nitrethyltoluidine, crystallises from alcohol in long straw-yellow needles, and from benzene in dense prisms, melting at  $115-116^{\circ}$ ; it appears to be identical with v. Romburgh's dinitroparacresylethyl-nitramine (*Rec. Trav. Chim.*, 3, 392). *Metanitroparamethylethyltoluidine*,

$\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NHMe}$ , is obtained from nitrotoluidine, methyl iodide, and methyl alcohol; it crystallises from alcohol in red needles and from benzene in plates, and melts at  $84-85^\circ$ . The corresponding *amido-derivative* forms four-sided plates melting at  $43-44^\circ$ . *Dinitromethyltoluidine* is prepared in the same way as the corresponding ethyl-derivative; it crystallises from alcohol in long bright red needles, melting at  $129^\circ$ . *Nitrosodinitromethyltoluidine*,



crystallises from alcohol in pale yellow needles, and from benzene in sulphur-coloured crystals melting at  $125^\circ$ . *Trinitromethyltoluidine* crystallises from alcohol in light yellow needles, from benzene in large well-formed prisms, melting at  $137-138^\circ$ . This was also obtained by v. Romburgh (*loc. cit.*).  
A. K. M.

### Condensation of Chloral Hydrate with Tertiary Amines.

By P. BOESSNECK (*Ber.*, 18, 1516—1521).—*Dimethamidophenyl trichloromethyl carbinol*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{CCl}_3)\cdot\text{OH}$ , is formed in small quantity by the action of chloral on dimethylaniline, together with the methylated pentaphenylethane described by O. Fischer (*Abstr.*, 1879, 53). It crystallises in white plates, melts at  $111^\circ$  with partial decomposition; the hydrochloride forms colourless needles. Aqueous potash decomposes it with formation of chloroform and a substance crystallising in colourless plates, melting at  $73^\circ$ , and distilling readily with steam. This is probably one of the dimethamidobenzaldehydes, and is formed much more readily by employing alcoholic instead of aqueous potash.  
A. J. G.

### General Method for Determining the Constitution of Aromatic Diamines.

By E. LELLMANN (*Annalen*, 228, 248—250).—Orthodiamines may be distinguished from the corresponding para- and meta-derivatives by the following process:—An aqueous solution of ammonium thiocyanate is added to the diamine, and the mixture evaporated to dryness. The residue is heated at  $120^\circ$  for one hour. It is then thoroughly washed with water and treated with an alkaline solution of lead acetate; no reaction takes place with orthodiamines, but meta- and para-diamines yield a black precipitate of lead sulphide.

II. The alcoholic solution of the diamine is treated with allyl thiocarbimide and the product melted. In the case of an *orthodiamine*, the compound resolidifies, forming a crystalline mass. If it is heated until decomposition ensues, the solid residue, on recrystallisation from alcohol, will not exhibit any change when treated with an alkaline solution of lead acetate.

Under similar treatment, the *metadiamine* compound remains liquid after it has been melted, and is not decomposed by exposure to a temperature  $5^\circ$  above its melting point. The *para* compound melts, and is entirely decomposed.  
W. C. W.

**New Toluylenediamine.** By E. LELLMANN (*Annalen*, 228, 243—247).—The new nitrotoluidine (described on p. 974) is converted into the diamidotoluene,  $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2)_2$  [1 : 2 : 3], when reduced with tin

and hydrochloric acid. By the action of ammonium thiocyanate on the diamine, toluylene thiocarbamide,  $C_6H_3Me:N_2H_2:CS$ , is obtained in minute crystals. This substance dissolves in soda-lye, but on boiling the alkaline solution with lead acetate no precipitate of lead sulphide is produced.

*Diallyltoluylenedithiocarbamide* crystallises in silky needles, insoluble in water, but freely soluble in most other solvents. It melts at  $152^\circ$ , splitting up into diallylthiocarbamide and toluylenethiocarbamide.  
W. C. W.

### Chemical Behaviour of Aromatic and Fatty Diamines.

By E. LELLMANN and E. WÜRTNER (*Annalen*, 228, 199—243).

I. *Di-additive Products of Aromatic Diamines and Thiocarbimides*.—*Diphenylorthophenylenedithiocarbamide*,  $(NHPh \cdot CS \cdot NH)_2C_6H_4$ , is deposited as a crystalline precipitate when phenylthiocarbimide is added to an alcoholic solution of orthophenylenediamine, and the mixture gently warmed. It is soluble in alcohol and glacial acetic acid, sparingly soluble in benzene, and insoluble in ether. At  $170^\circ$  it splits up into diphenylthiocarbamide and orthophenylenethiocarbamide.

*Diallylorthophenylenedithiocarbamide*,  $(C_3H_5 \cdot NH \cdot CS \cdot NH)_2C_6H_4$ , crystallises in white needles, which dissolve freely in alcohol and glacial acetic acid, but sparingly in ether and benzene. The compound melts at  $158$ — $160^\circ$  with decomposition, yielding orthophenylenethiocarbamide and diallylthiocarbamide.

*Diphenylmetaphenylenedithiocarbamide*,  $(NHPh \cdot CS \cdot NH)_2C_6H_4$ , forms a grey powder, melting at  $161^\circ$ . It dissolves in caustic soda and in acetic acid, but is insoluble in ether, benzene, and alcohol. When heated at  $160$ — $185^\circ$  it splits up into diphenylthiocarbamide and other products.

*Diallylmetatoluylenedithiocarbamide*,  $(C_3H_5 \cdot NH \cdot CS \cdot NH)_2C_6H_3Me$ , is soluble in alcohol, but almost insoluble in ether and benzene. It melts at  $150.5^\circ$ , with slight decomposition.

*Diphenylparatoluylenedithiocarbamide* is almost insoluble in the ordinary solvents. It melts at  $181^\circ$ , decomposing into diphenylthiocarbamide and other products.

*Diallylparatoluylenedithiocarbamide*,  $(C_3H_5 \cdot NH \cdot CS \cdot NH)_2C_6H_3Me$ , crystallises in prisms, which are soluble in alcohol and in acetic acid. It melts at  $175.5^\circ$  with decomposition, but the products of decomposition were not isolated.

*Mono-additive Products of Phenylenediamine and Phenylthiocarbamide*.—*Monorthamidodiphenylthiocarbamide*,



is best prepared by the action of phenylthiocarbimide on an excess of the diamine dissolved in benzene. The product crystallises in white plates, and also in colourless prisms; it is soluble in alcohol and acetic acid. It begins to decompose at  $141^\circ$ , forming aniline and orthophenylenethiocarbamide.

*Monometamidodiphenylthiocarbamide*,  $NHPh \cdot CS \cdot C_6H_4 \cdot NH_2$ , is obtained in the form of a yellow amorphous powder, and also in colourless prisms. The carbamide dissolves freely in alcohol and acetic acid.

When heated in a capillary tube, a slight sublimate begins to form at 110°, and the substance melts at about 148—153°, with partial decomposition.

*Monoparamidodiphenylthiocarbamide* crystallises in prisms of a reddish colour, soluble in acetic acid. It begins to decompose at 163° into aniline and paraphenylenethiocarbamide.

The *mono-additive products of phenylenediamines and phenyl cyanate* are decomposed by heat, yielding phenylenecarbamides and aniline; for instance, monorthamidodiphenylcarbamide yields orthophenylenecarbamide, and the meta- and para-derivatives yield meta- and paraphenylenecarbamide respectively. Paraphenylenecarbamide forms a brown powder, insoluble in the usual solvents. It does not melt at 320°.

*Preparation of Trimethylene and Tetramethylenediamine.*—Trimethylenediamine,  $C_3H_6(NH_2)_2$ , is formed by the action of a large excess of alcoholic ammonia on trimethylene bromide (compare E. Fischer and Koch, Abstr., 1884, 1289). Attempts to obtain tetramethylenediamine by the reduction of the nitrile did not yield satisfactory results.

*Trimethylenediamine thiocyanate*,  $C_3H_6(NH_3 \cdot SCN)_2$ , prepared by the action of aqueous thiocyanic acid on the diamine, is freely soluble in alcohol and in water, and melts at 102°. It is decomposed by prolonged heating at 140° into trimethylenethiocarbamide and ammonium thiocyanate. *Trimethylenethiocarbamide*,  $C_3H_6 < \begin{smallmatrix} NH \\ NH \end{smallmatrix} > CS$ , crystallises in white needles, freely soluble in water, alcohol, chloroform, and benzene. It melts at 198°. Allylthiocarbimide unites with ethylenediamine, forming *diallylethylenedithiocarbamide*,



a thick oily liquid, miscible with alcohol and chloroform.

*Diphenylethylenedithiocarbamide* forms white scales, insoluble in alcohol, ether, and benzene. It melts at 193°, splitting up into diphenylthiocarbamide and thiocarbamilide.

*Diphenyltrimethylenedithiocarbamide* melts at 115°, and is freely soluble in alcohol, ether, benzene, and acetic acid. W. C. W.

**Decomposition-products of Acetanilide Hydrochloride.** By E. NÖLTING and E. WEINGÄRTNER (*Ber.*, 18, 1340—1343).—Acetanilide hydrochloride is prepared by saturating a solution of acetanilide in acetone with hydrogen chloride; the salt crystallises out and is dried in a stream of dry air; it is resolved into its constituents by cold water. On exposure to the air it absorbs water and is decomposed into aniline hydrochloride and acetic acid. By heating at 250° for half an hour in a sealed tube, acetic acid separates and ethylenediphenylamidine is formed. Heated for six hours at 280° flavaniline is formed in small quantities, and on heating for ten hours at 280—300° a tarry mass is formed, from which a mixture of quinoline bases and aniline was obtained. On removing the aniline and again distilling, a substance boiling at 265—268° is obtained having the constitution  $C_{11}H_{11}N$ : an ethyl- or dimethyl-quinoline; the platinochloride,  $(C_{11}H_{11}N)_2H_2PtCl_6$ , was prepared; it forms yellow scales, the methiodide melting at 203° and the chlorate were also obtained. From a

second fraction distilling between  $270^{\circ}$  and  $280^{\circ}$  a platinochloride was obtained and purified by repeated recrystallisation; its analysis showed it to be the salt of a trimethylquinoline. Both the above-mentioned quinoline bases were liquid, had the characteristic quinoline odour, and gave a yellow coloration when heated with zinc chloride and phthalic anhydride. The yield is very small.

The residue left after the distillation of the volatile quinoline bases is a waxy mass, and probably consists of polymerised quinolines or oxyquinolines. An unsuccessful attempt was made to obtain these bases by heating aniline with acetic chloride, and aniline hydrochloride with acetic anhydride, mere traces of quinoline-derivatives being formed.

Acetoparatoluide, like acetanilide, also yields a hydrochloride having the constitution  $(C_6H_4Me \cdot NHAc)_2HCl$ .

Benzanilide also forms a hydrochloride, but it is very unstable; on heating it at  $300^{\circ}$  benzoic acid and benzenyldiphenylamide are formed. A. P.

**Action of Phenyl Isocyanate on Amido-compounds.** By B. KÜHN (*Ber.*, **18**, 1476—1479; compare p. 260).—When equal molecular proportions of benzanilide and phenyl cyanate are heated together at  $180$ — $200^{\circ}$  for four hours, *benzenyldiphenylamidine*,  $NPh : CPh \cdot NHPh$ , is produced melting at  $145$ — $146^{\circ}$ . The reaction is, however, not a general one. On heating formanilide with phenyl cyanate at  $180^{\circ}$ , phenylcarbylamine and carbanilide are formed. *Benznaphthalide* and carbanil when heated at  $180^{\circ}$  yield resinous products. When *acetanilide* is heated at  $200^{\circ}$  with phenyl cyanate, diphenylcarbamide is obtained together with a yellow substance which does not melt, is insoluble in the ordinary solvents, and crystallises in microscopic prisms from boiling nitrobenzene; the nature of this substance is not yet understood.

An ethereal solution of toluylenediamine reacts readily with phenyl cyanate (2 mols.) with formation of *diphenyltoluylenedicarbamide*,  $C_7H_6(NH \cdot CO \cdot NHPh)_2$ ; this is insoluble in water, alcohol, ether, benzene, and chloroform, dissolves very sparingly in glacial acetic acid, readily in hot aniline, with decomposition, however, and separation of phenyl cyanate; it melts above  $300^{\circ}$ . *Diphenylphenylenedicarbamide*,  $C_6H_4(NH \cdot CO \cdot NHPh)_2$ , is obtained in the same way from *metaphenylenediamine*; it is likewise insoluble in the usual solvents, and is decomposed by aniline. *Diphenyldiphenylenedicarbamide*,  $C_{12}H_8(NH \cdot CO \cdot NHPh)_2$ , is prepared from benzidine (1 mol.) and phenyl cyanate (2 mols.), and is soluble only in concentrated sulphuric acid and in aniline, crystallising from the latter in concentrically-grouped needles melting at above  $300^{\circ}$ . A. K. M.

**Phthalimidine.** By C. GRAEBE (*Ber.*, **18**, 1408).—This name is assigned to the base  $C_8H_7NO$  described by the author (this vol., p. 165), instead of the name phthalidine.

**Derivatives of Dicyanophenylhydrazine.** By J. A. BLADIN (*Ber.*, **18**, 1544—1551).—Dicyanophenylhydrazine was prepared by Fischer (*Abstr.*, 1878, 310), who ascribed to it the formula



$\text{NH}:\text{C} < \begin{smallmatrix} \text{C}:(\text{NH}) \\ \text{---NPh---} \end{smallmatrix} > \text{NH}$ ; the author's results, however, and especially the formation of an anhydro-compound, accord better with the constitution  $\text{NH}_2\text{NPh}\cdot\text{C}(\text{NH})\cdot\text{CN}$ .

When heated with acetic anhydride dicyanophenylhydrazine yields not, as was expected, an acetyl compound, but an anhydro-compound of this latter of the formula  $\text{C}_{10}\text{H}_8\text{N}_4 = \begin{smallmatrix} \text{N}\cdot\text{NPh} \\ \parallel \\ \text{CMe}\cdot\text{N} \end{smallmatrix} > \text{C}\cdot\text{CN}$ . It crystallises

in hard, colourless prisms, melts at  $108-108.5^\circ$ , is sparingly soluble in water, and has feebly basic properties. When heated with alcoholic

potash it is converted into an acid of the formula  $\begin{smallmatrix} \text{N}\cdot\text{NPh} \\ \parallel \\ \text{CMe}\cdot\text{N} \end{smallmatrix} > \text{C}\cdot\text{COOH}$ .

This crystallises in colourless tables, is readily soluble in hot water and alcohol, sparingly soluble in ether, and melts at  $176-177^\circ$  with decomposition into carbonic anhydride and an oil,  $\text{C}_8\text{H}_8\text{N}_3$ , which boils at about  $240^\circ$ , and has a peculiar aromatic odour and basic properties.

When heated with excess of propionic anhydride, dicyanophenylhydrazine forms a similar anhydro-compound,  $\text{C}_{11}\text{H}_{10}\text{N}_4$ , melting at  $37.5-38^\circ$ ; it is sparingly soluble in water, readily soluble in ether and alcohol. With formic acid, dicyanophenylhydrazine yields the formyl compound  $\text{CHO}\cdot\text{NH}\cdot\text{NPh}\cdot\text{C}(\text{NH})\cdot\text{CN}$  as a colourless substance melting at  $192.5-193.5^\circ$ .

By the action of nitrous acid on dicyanophenylhydrazine a grey substance crystallising in needles is first formed; this is very unstable and readily resinifies; when heated with water it melts to a brown oil which solidifies on cooling. On recrystallisation this is obtained in long colourless needles of the formula  $\text{C}_8\text{H}_8\text{N}_6$ ; it melts at  $55.5-56^\circ$ , is sparingly soluble in water, readily soluble in alcohol and ether.

A. J. G.

**Glucovanillin and Glucovanillyl Alcohol.** By F. TIEMANN (*Ber.*, 18, 1595—1600).—The author and Reimer described under the name of saccharovanillic acid a substance obtained by the oxidation of coniferin (this Journal, 1875, 1199); as this substance is undoubtedly a dextrose-derivative the name glucovanillic acid is now substituted for the former title.

*Glucovanillin*,  $\text{COH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{O}\cdot\text{C}_8\text{H}_{11}\text{O}_5$  [1 : 3 : 4], can be obtained by the moderated action of potassium permanganate on coniferin, but is best prepared by mixing aqueous solutions of chromic anhydride and coniferin, and allowing the mixture to remain for some days at the summer temperature. It crystallises in white needles and melts, when pure, at  $192^\circ$ , a very minute amount of impurity suffices, however, to lower the fusing point  $8-10^\circ$ . It is insoluble in ether, moderately soluble in water, less soluble in alcohol. It does not reduce Fehling's solution in the cold nor on gentle heating; emulsion or dilute acids resolve it into dextrose and vanillin. It has a rotatory power  $[\alpha]_D = 66.90$ . When oxidised it yields glucovanillic acid.

*Glucovanillyl alcohol*,  $\text{HO}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{O}\cdot\text{C}_8\text{H}_{11}\text{O}_5 + \text{H}_2\text{O}$ , is prepared by heating an aqueous solution of glucovanillin with sodium amalgam; it crystallises in white needles, melts at  $120^\circ$ , is readily soluble

in water and alcohol, nearly insoluble in ether. It dissolves in strong sulphuric acid with a beautiful red-violet colour. Emulsin converts it into dextrose and vanillyl alcohol. Its rotatory power is somewhat less than that of glucovanillin.

Vanillyl alcohol melts at  $115^{\circ}$ ; the melting point formerly given (*Ber.*, 9, 415) is too low. A. J. G.

**Conversion of the Three Nitrilanines into Nitrobenzoic Acids.** By T. SANDMEYER (*Ber.*, 18, 1492—1496).—Paranitraniline is treated with dilute hydrochloric acid and a solution of sodium nitrite, and the resulting diazo-product gradually added to a hot ( $90^{\circ}$ ) solution of potassium cyanide and copper sulphate (for proportions see p. 149). The whole is then boiled for a few minutes, well cooled, and the nitrobenzonitrile collected; this is saponified by boiling with aqueous soda. An alcoholic solution must not be employed, as it acts as a reducing agent. The yield of pure paranitrobenzoic acid was 63 per cent. of that required by theory. Meta- and ortho-nitrilanines may be similarly converted into the corresponding nitrobenzoic acids.

By means of the method previously described (*loc. cit.*) for substituting an amido-group by a halogen, metanitrilaniline may be converted into metanitrobenzobromobenzene. By the reduction of this, metabromaniline is obtained which, when treated as above, yields bromobenzoic acid. On nitrating this and reducing the product, bromamidobenzoic acids are obtained which, when boiled with aqueous soda and zinc-dust, are converted into anthranilic acid.

A. K. M.

**Conversion of the Three Amidobenzoic Acids into Phthalic Acids.** By T. SANDMEYER (*Ber.*, 18, 1496—1500).—This is effected by means of the reaction described in the last Abstract. Whilst trying to purify the nitrile from paramidobenzoic acid, it was found to have taken up a molecule of water and to have become converted into *terephthalamic acid*,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CONH}_2$ ; this is sparingly soluble in cold, readily in hot water, in alcohol, ether, and warm acetic acid; it crystallises in indistinct microscopic scales melting at  $214^{\circ}$ . On boiling it with soda, ammonia is evolved and terephthalic acid produced.

Metamidobenzoic acid yielded *metacyanobenzoic acid*,  $\text{CN}\cdot\text{C}_6\text{H}_3\cdot\text{COOH}$ , which is easily purified; it is readily soluble in ether, alcohol, and hot water, and crystallises from the latter in clusters of microscopic needles, melting at  $217^{\circ}$ . It is readily saponified to isophthalic acid. From *anthranilic acid* the author obtained an oily compound which has not been identified, and phthalimide. The latter formed long thin needles melting at  $227^{\circ}$ , and yielded phthalic acid on saponification.

A. K. M.

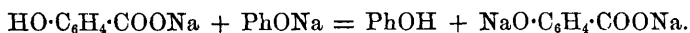
**Simple Method for Preparing Hippuric Acid and Allied Compounds.** By J. BAUM (*Zeit. physiol. Chem.*, 9, 465—468).—The author finds that various synthetical reactions with benzoic chloride are not affected by the presence of water; and of these, that its reaction with glycocine proceeds with perfect smoothness when it is added to the strong aqueous solution of the latter. After adding the chloride in excess the solution is made alkaline with sodium hydroxide,

then acidified, and the hippuric acid separated from benzoic acid, and isolated in the usual way. By this method the author obtained from 2 grams of glycocine  $1\frac{1}{2}$  grams of the pure hippuric acid melting at  $187.5^{\circ}$ . Benzoylalanine was prepared in similar manner.

Tyrosine in alkaline solution, when treated with the chloride, was converted into a polysubstituted benzoyl-derivative, which is under investigation. The author is investigating the reaction of benzoic chloride with various amido- and imido-acids under similar conditions (comp. Curtius, Abstr., 1884, 1347). C. F. C.

**Kolbe's Synthesis of Salicylic Acid.** By R. SCHMITT (*J. pr. Chem.* [2], **31**, 397—411).—Kolbe finally interpreted his process for the synthesis of salicylic acid as a reaction between 1 mol. of carbonic anhydride and 2 mols. of sodium phenoxide with production of disodium salicylate and phenol, thus:  $-2\text{PhONa} + \text{CO}_2 = \text{NaO}\cdot\text{C}_6\text{H}_4\cdot\text{COONa} + \text{PhOH}$ . Baumann, on the other hand, from analogy of the transformation of potassium phenylsulphate into potassium paraphenolsulphonate, supposed that in the preparation of salicylic acid sodium phenyl carbonate was at first formed, and was subsequently converted into sodium salicylate, thus:  $-\text{PhONa} + \text{CO}_2 = \text{PhO}\cdot\text{COONa} = \text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{COONa}$ , an hypothesis, in fact, confirmed by Hentschel, who showed that diphenyl carbonate and sodium phenate gave sodium salicylate.

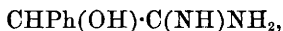
In the present paper the author shows that sodium phenoxide absorbs the quantity of carbonic anhydride theoretically required for its conversion into sodium phenyl carbonate, provided that all the materials are perfectly dry. The substance thus obtained is readily decomposed by water with evolution of carbonic anhydride, thus:  $2\text{PhO}\cdot\text{COONa} + \text{H}_2\text{O} = \text{CO}_2 + \text{PhOH} + \text{NaHCO}_3 + \text{PhONa}$ ; when heated in a closed tube at  $120-130^{\circ}$  it is practically completely transformed into sodium salicylate. The formation of disodium salicylate in Kolbe's process is experimentally shown to be the result of the action of sodium phenoxide on the monosodium salicylate. The successive reactions in Kolbe's process are then (1) the formation of sodium phenyl carbonate,  $\text{PhONa} + \text{CO}_2 = \text{PhO}\cdot\text{COONa}$ ; (2) the conversion of this substance into sodium salicylate,  $\text{PhO}\cdot\text{COONa} = \text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{COONa}$ ; and (3) the formation of disodium salicylate and phenol,



V. H. V.

**Derivatives of Mandelic Acid.** By C. BEYER (*J. pr. Chem.* [2], **31**, 382—397).—By passing hydrogen chloride into a solution of the nitrile of mandelic acid and alcohol in ether, mandelic acid imido-ether hydrochloride,  $\text{CHPh}(\text{OH})\cdot\text{C}(\text{OEt})\cdot\text{NH}_2\cdot\text{HCl}$ , is produced. This substance crystallises in needles melting at  $120^{\circ}$ ; by heating it is decomposed into mandelamide and ethyl chloride; by potash the hydrochloric acid is removed with production of the free *hydrimido-ether*,  $\text{CHPh}(\text{OH})\cdot\text{C}(\text{NH})\text{OEt}$ , which crystallises in long needles melting at  $72^{\circ}$ ; it quickly turns brown on exposure to the air with evolution of ammonia. By the action of ammonia on an alcoholic solution of the above-mentioned hydrochloride, *phenylhydroxyacetamidine hydro-*

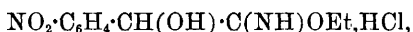
*chloride*,  $\text{CHPh}(\text{OH})\cdot\text{C}(\text{NH})\text{NH}_2\cdot\text{HCl}$ , is formed, which crystallises in large colourless prisms melting at  $214^\circ$ . The hydrogen chloride is removed by potash to form the free *amidine*,



crystallising in grouped needles, melting at  $100^\circ$ , readily soluble in alcohol and ether.

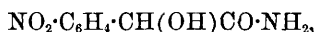
The imido-ether hydrochloride dissolves in water with separation of *ethyl mandelate*,  $\text{CHPh}(\text{OH})\cdot\text{COOEt}$ ; this substance is a heavy, colourless, refractive oil, smelling like jasmine, and boiling at  $253^\circ$ .

*Metanitrophenylhydroxyacetimido-ether hydrochloride*,



prepared from nitrobenzaldehyde by a similar process to that described above, crystallises in pale yellow needles, melting at  $129^\circ$  with decomposition into nitromandelamide and ethyl chloride.

The free imido-ether crystallises in microscopic needles, which melt at  $84^\circ$ ; it is readily soluble in alcohol and ether. From the hydrochloride by decomposition with water, *ethyl metanitromandelate* is formed; it crystallises in glistening needles melting at  $63^\circ$ ; it is readily saponified with formation of nitromandelic acid, which crystallises in glassy rhombohedra melting at  $120^\circ$ ; soluble in water, ether, and alcohol. Its ammonium salt crystallises in needles, whose solution in water gives white precipitates with silver nitrate, lead acetate, and ferrous sulphate. The *amide*,



obtained by the action of ammonia on the ethyl salt, crystallises in prisms.

V. H. V.

**Action of Carbonic Anhydride on Sodium Acetanilide. New Synthesis of Dicarboxylic from Monocarboxylic Acids.** By R. SEIFERT (*Ber.*, 18, 1358—1361).—The sodium acetanilide employed was prepared by treating a concentrated alcoholic solution of sodium ethoxide with acetanilide, and freeing from alcohol by distilling on an oil-bath in a stream of hydrogen.

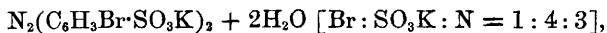
By saturating sodium acetanilide with carbonic anhydride, sodium acetylphenylcarbamate,  $\text{NPhAc}\cdot\text{COONa}$ , is formed; it is decomposed by the action of the water into acetanilide and sodium carbonate; by heating at  $100^\circ$ , carbonic anhydride is given off; by heating at  $130$ — $140^\circ$  for 5—6 hours in a sealed tube, and treating the mass thus obtained with a slight excess of concentrated hydrochloric acid, carbonic anhydride is given off and a crystalline compound is formed, part of which is soluble in dilute ammonia, from which solution on acidifying, a precipitate of malonanilic acid is formed; by slowly crystallising from a concentrated aqueous solution it separates in large lustrous monoclinic crystals, exhibiting a curious cross-like mark on the terminal planes which passes through the whole crystal. When heated at  $135^\circ$  until no more carbonic anhydride is given off, the whole of the malonanilic acid is converted into acetanilide. By drying the residue which was insoluble in ammonia, obtained in the prepara-

tion of malonanilic acid, extracting the acetanilide with ether, and recrystallising the insoluble residue from boiling glacial acetic acid, colourless needles melting at  $220^{\circ}$  are obtained; this substance is probably malonanilide, it is only slightly soluble in alcohol, and is insoluble in water and ether. A. P.

**Oxidation of Amidobenzenesulphonic Acids by Potassium Permanganate.** By H. LIMPRICHT (*Ber.*, 18, 1414—1425).—In the oxidation of these acids and of their bromo-derivatives, by potassium permanganate ( $\frac{3}{4}$  mol.), Rodatz (*Abstr.*, 1883, 478) obtained 33 per cent. of the theoretical quantity of the azosulphonic acid. The reaction is, however, not complete, unless 4.7 mols. of potassium permanganate are used, when the yield of azo-acid is only 25 per cent. The author found by quantitative experiments that in this case about 75 per cent. of the total carbon, nitrogen, and sulphur are given off as oxalic acid, carbonic anhydride, ammonia and sulphuric acid. Experiments were made with the three isomeric amidobenzenesulphonic acids, and the following compounds obtained:

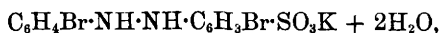
*Parazoxybenzenemonosulphonic acid*,  $\text{PhN} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{N} \end{array} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ , forms rosettes of red scales, very readily soluble in water, and melts below  $100^{\circ}$ . When strongly heated it swells up, and burns without leaving an ash. The *potassium salt*, with 2 mols.  $\text{H}_2\text{O}$ , is described. *Meta-zoxybenzenemonosulphonic acid* crystallises in reddish-brown plates which, when treated with a little alcohol, fall into an amorphous powder. It melts at  $60$ — $70^{\circ}$ . The *potassium salt* was prepared. *Orthoazoxybenzenesulphonic acid* was not prepared; the *potassium salt* forms a reddish-brown hygroscopic powder.

*Amidomonobromobenzenesulphonic acid*,  $[\text{SO}_3\text{H} : \text{NH}_2 : \text{Br} = 1 : 3 : 4]$ , yields on oxidation, &c., the following compounds: *Potassium dibromazobenzenesulphonate*,



forms ruby-coloured lustrous plates, soluble in 10—12 parts of water, insoluble in alcohol. *Potassium monobromazoxybenzenesulphonate*,  $\text{Ph}\cdot\text{N}_2\text{O}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{SO}_3\text{K} + 2\text{H}_2\text{O}$ , forms small red hexagonal plates, soluble in 2—3 parts of water.

From the products of oxidation of the dibromamidosulphonic acids, the author obtained, besides the tetrabromazobenzenedisulphonic acids described by Rodatz, the following potassium salts: *Potassium azoxydibromobenzenesulphonate*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\text{O}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{SO}_3\text{K} + 2\text{H}_2\text{O}$ , derived from the acid  $[\text{Br}_2 : \text{NH}_2 : \text{SO}_3\text{H} = 1 : 3 : 6 : 4]$ , forming very small pale yellow scales, soluble in 2 parts of water and in 8—10 parts of alcohol. *Potassium hydrazodibromobenzenesulphonate*,



from the acid  $[\text{Br}_2 : \text{NH}_2 : \text{SO}_3\text{H} = 1 : 5 : 6 : 3]$ , forming tufts of long white needles. N. H. J. M.

**Azobenzenethio-sulphonic Acids and Azobenzenesulphinic Acids.** By H. LIMPRICHT (*Ber.*, 18, 1468—1475).—This is a con-

tinnation of Heffter's and Paysan's researches (Abstr., 1884, 453 and 454). When metazobenzenedisulphonic chloride is gradually added to a saturated solution of barium hydrosulphide, barium hydrazobenzenedithiodisulphonate separates, whilst on concentrating the liquid, barium azobenzenedithiodisulphonate is obtained; if ammonium hydrosulphide be employed the reaction is more energetic, and on expelling the excess of sulphide by evaporation, and finally heating the product with barium hydroxide as long as ammonia is given off, barium azobenzenedithiodisulphonate and azobenzenemonothiodisulphonate are produced. The hydrazo-compound is converted by atmospheric oxygen into the azo-compound, and the azobenzenedithiodisulphonates are on recrystallisation gradually converted into azobenzenemonothiodisulphonate with separation of sulphur.

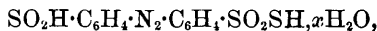
*Metahydrazobenzenedithiodisulphonic acid,*



separates as a bulky yellowish-white amorphous precipitate, on adding hydrochloric or concentrated acetic acid to a hot dilute solution of the barium salt. The barium salt,  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}_4\text{O}_4\text{Ba} + 2\text{H}_2\text{O}$ , is obtained as a white powder by the action of hydrogen barium sulphide on nitrobenzenesulphonic chloride; if suspended in water and digested at a gentle heat with mercuric oxide, barium azobenzenemonothiodisulphonate,  $\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{Ba}$ , and mercuric sulphide are produced. By the action of potassium permanganate on barium hydrazobenzenedithiodisulphonate, potassium azobenzenedisulphonate,  $\text{N}_2(\text{C}_6\text{H}_4\cdot\text{SO}_3\text{K})_2$ , is formed.

*Metazobenzenedithiodisulphonic acid*,  $\text{N}_2(\text{C}_6\text{H}_4\cdot\text{SO}_2\text{SH})_2 + 1\frac{1}{2}\text{H}_2\text{O}$  (?), is precipitated from its salts by glacial acetic acid, mineral acids decomposing it; it forms a bulky, bright yellow, amorphous mass, almost insoluble in water and alcohol; it darkens when heated and melts between  $91^\circ$  and  $93^\circ$ . The barium salt,  $\text{N}_2\text{C}_{12}\text{H}_{10}\text{S}_4\text{O}_4\text{Ba} + 5\text{H}_2\text{O}$ , sodium, and ammonium salts are described; they are converted by yellow ammonium sulphide into hydrazobenzenedithiodisulphonates, and by permanganate into azobenzenedisulphonate.

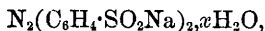
*Metazobenzenemonothiodisulphonic acid,*



is precipitated from its salts by mineral acids as a bulky yellow and apparently amorphous precipitate, very sparingly soluble in water and alcohol; it melts under  $100^\circ$ . The barium salt is obtained on evaporating the solution of barium hydrazo- and azobenzenedithiodisulphonates; the potassium and sodium salts are also described; they are converted by potassium permanganate into azobenzenedisulphonates. When azobenzenemonothiodisulphonic acid is precipitated by the addition of an acid to a solution of a salt and ammonia then added to the filtrate, a reddish-brown amorphous precipitate is obtained, which has the same composition as azobenzenemonothiodisulphonic acid, but has basic properties; it is readily soluble in acids, and yields a hydrobromide of the composition



*Metazobenzenedisulphinic acid*,  $N_2(C_6H_4 \cdot SO_2H)_2$ , is obtained by the action of sodium amalgam on an aqueous solution of an azobenzene-monothiodisulphonate or of an azobenzenedithiodisulphonate; the addition of a mineral acid throws it down as a bulky, yellowish-white amorphous mass, insoluble in ether, sparingly soluble in cold, more readily in hot water and in alcohol. The sodium salt,

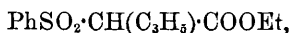


barium, calcium, and lead salts are described. The sulphinates are converted by potassium permanganate, Fehling's solution, iodine, or chlorine into azobenzenedisulphonates, and by ammonium sulphide into azobenzenedithiodisulphonates. When sulphinic acid is heated with concentrated hydrochloric, or hydrobromic, or with moderately dilute sulphuric acid at  $110^\circ$  in a sealed tube, about 2 per cent. is converted into an isomeric basic substance, which is precipitated on adding ammonia to the acid liquid; it forms a yellowish scaly mass, is sparingly soluble in water and in cold alcohol, readily in hot alcohol and insoluble in ether; the hydrochloride and hydrobromide are very soluble and decompose readily. By the action of stannous chloride and hydrochloric acid on the sulphinic acid, a base is produced which appears to have the same composition as hydrazobenzene-dithiodisulphonic acid, and which is probably related to benzene-sulphamine.

When parazobenzenedisulphonic chloride is added to hydrogen barium sulphide, *barium azobenzenedisulphinate* is precipitated whilst *barium azobenzenedithiodisulphonate* remains in solution. Parazobenzenedithiodisulphonic acid,  $N_2(C_6H_4 \cdot SO_2SH)_2$ , is precipitated from its salts as a bulky yellow mass, very sparingly soluble in water and alcohol; the barium salt,  $N_2C_{12}H_8S_4O_4Ba$ , and sodium salt,  $N_2C_{12}H_8S_4O_4Na_2, 4H_2O$ , are described. Parazobenzenedisulphinic acid,  $N_2(C_6H_4 \cdot SO_2H)_2$ , is also produced by the action of sodium amalgam on azobenzenedithiodisulphonic acid; it forms a yellow voluminous mass, very sparingly soluble in water and alcohol. The barium salt and sodium salt,  $N_2C_{12}H_8S_2O_4Na_2, 4H_2O$ , are described. A. K. M.

**Properties of Phenylsulphonacetates.** By A. MICHAEL and G. M. PALMER (*Amer. Chem. J.*, 7, 65—71).—Ethyl phenylsulphonacetate (comp. Abstr., 1884, 319) when heated with caustic potash at  $140^\circ$  yields phenylmethylsulphone,  $SO_2MePh$ ; when treated with sodium ethoxide and ethyl iodide *ethyl ethylphenylsulphonacetate*,  $PhSO_2 \cdot CHEt \cdot COOEt$ , is obtained; this melts at  $62^\circ$ , and when heated with alcoholic potash yields *propylphenylsulphone*,  $PhSO_2 \cdot CH_2Et$ , melting at  $45^\circ$ . It does not appear possible to introduce a second ethyl-group into the above mon-ethyl-derivative.

The corresponding *ethyl allylphenylsulphonacetate*,



is prepared in similar manner, it melts at  $64.5^\circ$ ; the study of the corresponding sulphone is incomplete.

Although it does not appear possible to introduce two ethyl-groups into ethyl phenylsulphonacetate, yet two benzyl-groups may be easily

introduced; ethyl dibenzylsulphonacetate,  $\text{PhSO}_2\cdot\text{C}(\text{CH}_2\text{Ph})_2\text{COOEt}$ , is decomposed by alkalis in the same way as the monobenzyl-derivative (*loc. cit.*), and yields *benzylcinnamic acid*,



melting at  $157^\circ$ ; the sodium salt is anhydrous, the silver salt only slightly soluble in water; when treated with sodium amalgam it is converted into *hydrobenzylcinnamic* or *dibenzylacetic acid*,



melting at  $87^\circ$ , and yielding a crystalline silver salt. These decompositions and reactions of ethyl phenylsulphonacetate exactly resemble those of ethyl acetoacetate. H. B.

**New Class of Sulphonic Acids of the Aromatic Series.** By A. SPIEGEL (*Ber.*, 18, 1479—1482).—The author finds that azo-dyes enter into combination with hydrogen sulphites. In the case of sulphonated azo-dyes soluble in water, the combination is effected in a warm aqueous solution, whilst an alcoholic solution is employed in the case of azo-dyes insoluble in water. The products obtained from red dyes yield yellow aqueous solutions, and those from blue azo-dyes, red solutions. The hydrogen sulphite compounds crystallise well, and the crystals are more or less dark in colour and show a metallic lustre; they are very stable towards dilute acids, but are decomposed by heat and by alkalis into the original dye and a sulphite; this latter property is made use of in dyeing; their general formula may be represented thus:  $\text{HXN}\cdot\text{NY}\cdot\text{SO}_3\text{Na}$ .

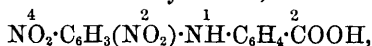
A different reaction takes place when azobenzene, hydrogen ammonium sulphite, and alcohol are heated together; in this case *amidodiphenylsulphamic acid*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_3\text{H}$ , is produced. The product is filtered, washed repeatedly with water and alcohol, dissolved in hot dilute sodium carbonate solution, again filtered and acidified, when the new compound is thrown down as a gelatinous mass. This benzidinesulphonic acid has pronounced acid properties and yields colourless crystalline alkali salts. It dissolves in concentrated sulphuric acid, but the solution at once begins to deposit crystals of benzidine sulphate; this property and the mode of formation of the acid, show that the sulphonic group must be united to the nitrogen and not directly to the nucleus.

Nitrosonaphthol reacts violently with hydrogen sulphites, and on acidifying the product a yellowish powder is precipitated; this is soluble in alkalis, and when heated with water at  $150^\circ$  yields naphthoquinol.

Certain nitro-compounds appear to yield similar reactions.

A. K. M.

**New Syntheses of Derivatives of Hydroacridine and Acridine.** By F. JOURDAN (*Ber.*, 18, 1444—1456).—When anthranilic and metachlororthamidobenzoic acids react with chlorodinitrobenzene, dinitrodiphenylamineorthocarboxylic acid,



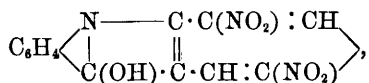
and the corresponding chlorine-derivative are produced. On treating



these products with reducing agents, not only are the nitro-groups reduced, but a molecule of water is also eliminated, and the resulting base has no longer acid properties, is not dissolved by hot aqueous alkalis, nor altered by boiling alcoholic potash; its solutions do not fluoresce. When it is heated with concentrated sulphuric acid, it is converted into an isomeric yellow dye. The constitution of the

new base is probably  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{C}(\text{NH}_2) : \text{CH} \\ \text{CO} \cdot \text{C} \cdot \text{CH} : \text{C}(\text{NH}_2) \end{array} \right\rangle$ , according to which it is a derivative of hydroacridine.

On heating dinitrodiphenylamineorthocarboxylic acid with concentrated sulphuric acid at 110–120°, water is likewise eliminated, but in this case a hydroxy-derivative of acridine,



appears to be formed. The corresponding amido-base is isomeric with and totally distinct from that mentioned above. The alcoholic solutions of the free base are of an intense yellowish-brown colour, and show a magnificent bright green fluorescence.

In order to obtain *dinitrodiphenylamineorthocarboxylic acid*, molecular proportions of anthranilic acid and chlorodinitrobenzene are dissolved in alcohol and heated in a reflux apparatus, with an excess of ammonia. The free acid crystallises in slender, orange-yellow needles melting at 262–264°; it is sparingly soluble in cold, more readily in warm alcohol and glacial acetic acid, almost insoluble in water, benzene, and light petroleum. It has marked acid properties, readily decomposes alkaline carbonates, and yields well crystallised salts.

*Chlorodinitrodiphenylamineorthocarboxylic acid* is prepared in the same way as the last compound, and forms slender reddish-yellow needles melting at 280–282°; it is more sparingly soluble than the last acid.

*Diamidohydroacridineketone*,  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{NH} \\ \text{CO} \end{array} \right\rangle \text{C}_6\text{H}_2(\text{NH}_2)_2$ , is obtained by the action of tin and alcoholic hydrochloric acid on dinitrodiphenylamineorthocarboxylic acid. The hydrochloride forms thin, colourless needles, sparingly soluble in cold, more readily in hot water; when dried over lime, it is anhydrous and contains 1 mol. HCl to 1 mol. base. The free base melts at 222–223°, dissolves readily in hot alcohol, less so in cold alcohol, and is almost insoluble in ether, benzene, and light petroleum; it is not attacked by boiling aqueous or alcoholic potash, nor by concentrated hydrochloric acid. With warm concentrated sulphuric acid, it yields the sulphate, whilst at a higher temperature a sulphonic acid is produced, which is converted by continued heating into the sulphonic acid of the isomeric diamidohydroxyacridine.

*Chlorodiamidohydroacridineketone*,  $\text{C}_6\text{H}_4\text{Cl} \left\langle \begin{array}{c} \text{NH} \\ \text{CO} \end{array} \right\rangle \text{C}_6\text{H}_2(\text{NH}_2)_2$ , obtained on reducing chlorodinitrodiphenylamineorthocarboxylic acid,

melts at  $230^{\circ}$ , is almost insoluble in cold, more readily in hot water, and is more sparingly soluble in hot alcohol than the last-described base. It resembles the latter in its behaviour to concentrated sulphuric acid; the sulphate is very sparingly soluble, the hydrochloride is sparingly soluble in cold, more readily in hot water, and insoluble in fuming hydrochloric acid.

Anthranilic acid reacts with dichlorodinitrobenzene,



yielding a *chlorodinitrodiphenylamineorthocarboxylic acid*.

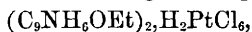


in which both nitro-groups are in the ortho-position to the imido-group, so that condensation cannot take place; it crystallises from glacial acetic acid in small thick red prisms, having a greenish lustre, melts at  $254\text{--}256^{\circ}$ , is insoluble in water, moderately soluble in hot alcohol and glacial acetic acid; its alkali salts and its barium salt crystallise well. *Chlorodiamidodiphenylaminecarboxylic acid*, obtained on reducing the nitro-compound, softens at about  $235^{\circ}$ , becoming completely fluid at  $245^{\circ}$  with decomposition. It is sparingly soluble in hot water and ether, almost insoluble in benzene and light petroleum, boiling alcohol forming the best solvent. When heated with concentrated sulphuric acid, carbonic anhydride is evolved.

The author has also tried the above reactions with other amido-acids and amido-ketones, and has found a ready method of ascertaining whether the amido-group in an aromatic amido-acid occupies the ortho-position to the carboxyl. When this is not the case, the amido-acid yields a dinitrodiphenylaminecarboxylic acid with chlorodinitrobenzene, which gives no condensation-product on reduction, but simply the corresponding amidodiphenylaminecarboxylic acid.

A. K. M.

**Carbostyryl.** By P. FRIEDLÄNDER and A. WEINBERG (*Ber.*, **18**, 1528—1533).—*Ethylpseudocarbostyryl*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} : \text{CH} \\ \text{NEt} \cdot \text{CO} \end{smallmatrix}$ , is obtained, together with ethylcarbostyryl by heating carbostyryl, alcohol, and ethyl iodide in a reflux apparatus, sodium ethoxide being gradually added. Ethylcarbostyryl alone distils when the mixture is steamed. Ethylpseudocarbostyryl crystallises in lustrous white needles, melts at  $53\text{--}55^{\circ}$ , is readily soluble in the ordinary solvents, except water, in which it is but sparingly soluble even on heating. The platinochloride,



crystallises in yellowish-red needles; the mercurichloride forms white needles. When bromine is added to a solution of ethylpseudocarbostyryl, a precipitate of yellowish-red needles forms; when exposed to air, these lose bromine, turn white, and then consist of a mixture of brom-substitution products. By the action of sodium amalgam on an alcoholic solution of ethylpseudocarbostyryl, a substance is obtained which seems to be identical with the ethyl-derivative of hydrocarbostyryl.

*Iodoquinoline* [ $I = 2'$ ] is obtained by the moderated action of hy-

driodic acid on the chloroquinoline prepared from carbostyryl. It crystallises in white needles, melts at  $52-53^{\circ}$ , and is decomposed on distillation. The hydriodide forms long, yellow needles. The platino-chloride,  $(C_9NH_6I)_2 \cdot H_2PtCl_6 + H_2O$ , crystallises in red needles.

*Phenylquinoliniumine*,  $C_9NH_6 \cdot NHPh$ , is obtained as hydrochloride by heating 2' chloroquinoline and aniline. The free base crystallises in lustrous white plates, melts at  $98^{\circ}$ , and boils at above  $360^{\circ}$ , nearly without decomposition. It yields soluble salts with acids; the chromate, however, is nearly insoluble. Ethylamine yields a similar compound, but diethylamine does not react with chloroquinoline. By the action of parabromaniline, a base,  $C_9NH_6 \cdot NH \cdot C_6H_4Br$ , is obtained, crystallising in silvery plates and melting at  $146^{\circ}$ .

*Tetrahydrodiquinoline*,  $C_9NH_6 \cdot NC_9H_{10}$ , is prepared by heating chloroquinoline with tetrahydroquinoline. It forms colourless crystals, melts at  $118^{\circ}$ , can be distilled, and dissolves in mineral acids with intense yellow colour.

A considerable portion of the paper is devoted to a criticism of the evidence as to the constitution of carbostyryl and related compounds, as to whether they should be regarded as lactam compounds containing the group  $NH \cdot CO$ , or lactim compounds containing the group  $N : C(OH)$ . On the whole, the authors seem to consider the latter hypothesis as the more plausible.

A. J. G.

**Derivatives of Triphenylcarbonyl Bromide.** By A. KÖLLIKER (*Annalen*, 228, 254—256).—The substance melting at  $217^{\circ}$ , which the author obtained, together with triphenylbromomethane, by the action of bromine on triphenylmethane (*Annalen*, 227, Part I), on closer investigation proves to be dibromanthracene.

W. C. W.

**Benz- $\beta$ -Naphthylamide and  $\beta$ -Dinaphthylamine.** By R. KLOPSCH (*Ber.*, 18, 1585—1587).—Cosiner described benz- $\beta$ -naphthylamide as crystallising in straw-yellow nodules, and melting at  $141-143^{\circ}$  (Abstr., 1881, 606). The author finds that the substance, when quite pure, forms colourless needles, and melts at  $157^{\circ}$ . On one occasion, when preparing this substance by the action of benzoic chloride on  $\beta$ -naphthylamine, the formation of phenylnaphthacridine was observed. As this compound is derived from  $\beta$ -dinaphthylamine, it seemed probable that this latter substance might be formed in the course of the reaction, by the hydrogen chloride eliminated acting on the  $\beta$ -naphthylamine, especially as the corresponding reaction is known to occur with  $\alpha$ -naphthylamine. An experiment confirmed this,  $\beta$ -naphthylamine being completely converted into  $\beta$ -dinaphthylamine by the action of hydrogen chloride for 10 minutes at  $190^{\circ}$ .

A. J. G.

**Terpinol.** By C. TANRET (*J. Pharm.* [5], 11, 506—510).—The author shows that the formula  $(C_{20}H_{16})_2 \cdot H_2O_2$  for terpinol should be rejected; that true terpinol, which boils at  $215-220^{\circ}$ , is a monohydrate of terebenthene  $(C_{20}H_{16}) \cdot H_2O_2$ , and that the product obtained, either by the action of dilute acid on terpinol, or by the action of alcoholic potash on terebenthene dihydrochloride, is only a mixture of the hydrocarbon  $C_{20}H_{16}$  with this monohydrate.

J. T.

**Reduction of Camphor to Borneol.** By C. L. JACKSON (*Amer. Chem. J.*, **6**, 404—407).—Immendorff's experiments (*Ber.*, **17**, 1036) have confirmed the statements of the author and Menke (*Abstr.*, 1884, 666), which had been disputed by Kachler and Spitzer (*Abstr.*, 1884, 754), that camphor is reduced to borneol if an alcoholic solution of the former is treated with sodium. Immendorff advised, however, the use of a larger proportion of sodium. The author has now repeated and substantially confirmed his former work with Menke, but finds that the best results are obtained by diminishing the quantity of alcohol used. The best yield of borneol (about 50—52 per cent. of the camphor acted on) is obtained as follows:—10 grams of camphor are dissolved in a beaker in 50 grams of common alcohol, and treated with 6 grams of sodium, cut into pieces of 0.1—0.2 gram. At first only two pieces of sodium should be added at a time, but after the fourth gram, a gram (cut in pieces as above) may be added at once. The liquid should be kept cool and frequently stirred, and a slow regular effervescence maintained. Towards the end of the reaction a drop or two of water may occasionally be added, to prevent the mass becoming pasty.

The author finds that, contrary to the statements of the text-books, an alcoholic solution of camphor is reduced by sodium amalgam, although the action is too slow to be of practical value.

L. T. T.

**Chitin.** By W. HALLIBURTON (*Ber.*, **18**, 1414).—A question of priority.

**Active Principle of Senna Leaves.** By R. STOCKMAN (*Pharm. J. Trans.* [3], **15**, 749—751).—The active principle of senna is cathartic acid, and it must be extracted without the application of heat or of hydrogen sulphide. Leaves which have been extracted with alcohol are moistened with dilute sulphuric acid, then again extracted with alcohol, the alcoholic extract precipitated with baryta, the barium salt decomposed, the acid converted into the lead salt, and this precipitated from solution by addition of alcohol and ether. The lead and barium salts are amorphous, and are decomposed by water into acid and basic salts. Cathartic acid is tasteless. Sodium cathartate administered internally to a rabbit caused violent diarrhoea and death in three hours, by inflammation of mucous membrane of the intestine; the urine gave a red coloration with potash. When injected it does not act, except on the urine. When boiled with acids, cathartic acid yields a glucose and a yellowish resinous acid substance of purgative properties, soluble in ether, alcohol, and alkalis (with red colour); insoluble in water. Cathartic acid is also decomposed by potash.

D. A. L.

**Destruction of Chlorophyll Solution by Light.** By J. REINKE (*Ann. Agronom.*, **11**, 232—236; from *Bot. Zeit.*, 1885, Nos. 5—9).—The prismatic spectrum was divided into seven bands, containing waves of definite range of wave-length, by means of seven cylindrical lenses interposed between the prism and the screen. The first band comprised rays of wave-length 750—710, and was separated from the

second band by rays of wave-length 710—700; the second band included wave-lengths 700—660, and was separated from the third by wave-lengths 660—650, and so on. Solutions of chlorophyll (from sunflower leaves) in alcohol and benzene were exposed for the same time to the light of each band, and the decoloration of the chlorophyll produced was measured by a photometric method. The mean decolorations were as follows:—Red band (wave-length 700—660), 100; orange (wave-length 650—610), 78; violet (wave-length 450—410), 72; yellow (wave-length 600—560), 58; blue (wave-length 500—460), 50; dark red (wave-length 750—710), 41; green (wave-length 550—510), 34. The action of the different coloured rays is therefore intimately related to the absorption-spectrum of chlorophyll, the maximum of decoloration falling between B and C, and coinciding with the maximum of absorption, and the curves being practically the same throughout their length.

J. M. H. M.

**Synthetical Pyridine and Piperidine Bases.** By A. LADENBURG (*Ber.*, 18, 1587—1590).—The author first corrects some erroneous statements previously made (*Abstr.*, 1884, 759) as to the bases obtained by distilling the additive compounds of pyridine with alkyl iodides. With regard to the two isomeric bases so obtained in each case, the base of lower boiling point yields picolinic acid only on oxidation, and therefore belongs to the  $\alpha$ -series, whilst the base of higher boiling point yields isonicotic acid only, and must belong to the  $\gamma$ -series.

Pyridine propyl iodide and pyridine isopropyl iodide both yield the same bases on distillation. The  $\alpha$ -base is not identical with conyryne, and is in all probability  $\alpha$ -isopropylpyridine. It boils at 158—159.5°. The platinochloride crystallises in monoclinic prisms,  $a : b : c = 0.9769 : 1 : 1.3848$ , and melts at 169—170°. The hydro-base boils at 159.5—160°; its hydrochloride melts at 208—210°, platinochloride at 193—193.5°, hydrobromide at 230—233°, hydriodide at 242—243°, and the cadmioidide crystallises in the monoclinic system,  $a : b : c = 2.0289 : 1 : 1.0054$ , and melts at 132—133°. The  $\gamma$ -base boils at 176—180°; its platinochloride melts at 203—204°.

Attempts to prepare  $\alpha$ -allylpyridine from pyridine allyl iodide have not been successful,  $\alpha$ -isopropylpyridine being formed in this case.

A. J. G.

**Action of Nitric Acid on Pyrrol Methyl Ketone.** By G. CIAMICIAN and P. SILBER (*Ber.*, 18, 1456—1466).—The authors recently described the formation of a nitropyrryl methyl ketone by the action of nitric acid on pyrrol methyl ketone at a low temperature (this vol., p. 810). They now find that four nitro-compounds are produced, namely,  $\alpha$ - and  $\beta$ -mononitropyrryl methyl ketones, dinitropyrrline, and dinitropyrryl methyl ketone. The first of these is the one previously described, and is the only one which does not show pronounced acid properties, so that it may be separated from the remaining three substances by agitating the ethereal solution with a concentrated solution of sodium carbonate.

Pyrrol methyl ketone has been obtained in large well-formed monoclinic crystals,  $\beta = 79^\circ 41'$ ;  $a : b : c = 2.91833 : 1 : 3.01735$ .

*$\alpha$ -Mononitropyrrolyl methyl ketone* is soluble in ether, benzene, chloroform, warm acetic acid, and in hot alcohol; it may be obtained perfectly white by boiling it with a dilute solution of chromic acid in acetic acid. Boiling hydrochloric acid has no action on it; fuming sulphuric acid dissolves it without decomposition, and it is also soluble in potash, ammonia, and in boiling sodium carbonate solution. It forms triclinic crystals;  $a : b : c = 0.729865 : 1 : 0.598890$ . By the action of bromine on a warm aqueous solution of the  $\alpha$ -nitroketone, *dibromomaleinimide*, boiling at  $225^\circ$ , is produced together with a trace of resin. The  $\alpha$ -nitro-derivative may be readily reduced by tin and hydrochloric acid to the corresponding amido-compound which, however, has not yet been obtained in the free state; the platino-chloride,  $C_6H_8N_2O, HPtCl_5$ , is described.

The sodium carbonate solution containing dinitropyrroline,  $\beta$ -nitropyrrolyl methyl ketone, and dinitropyrrolyl methyl ketone, is acidified with dilute sulphuric acid and repeatedly extracted with ether; the extract is evaporated, the residue left to crystallise, pressed, crystallised from boiling water, and afterwards from hot benzene. In this way a separation of the different compounds is effected. *Dinitropyrroline*,  $C_4NH_3(NO_2)_2$ , forms large yellowish-brown prisms melting at  $152^\circ$ , is soluble in ether, alcohol, acetic acid, hot benzene, and toluene, in hot water, and in hydrochloric and sulphuric acids. It behaves like an acid, dissolves in cold alkalis and in ammonia, with formation of salts, and also in alkaline carbonates. The silver and barium-derivatives,  $C_4H_4N_2O_6Ba$ , explode when heated. Dinitropyrroline forms well-formed crystals belonging to the trimetric system;  $a : b = 0.44123 : 1$ .

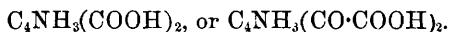
*Dinitropyrrolyl methyl ketone*,  $COMe \cdot C_4NH_2(NO_2)_2$ , crystallises from water in small yellow needles containing 1 mol.  $H_2O$ , which it loses at  $100^\circ$ ; it melts at about  $106$ – $107^\circ$ , or when dried, at  $114^\circ$ . It dissolves readily in ether, alcohol, and hot benzene, in the alkalis and alkaline carbonates.

*$\beta$ -Mononitropyrrolyl methyl ketone* may be separated from the last two compounds by means of its greater solubility in benzene, and is purified by crystallisation from hot water and subsequent sublimation. It crystallises in long needles melting at  $156^\circ$ , and is isomeric with the  $\alpha$ -compound above described, from which it differs in its physical and chemical properties; it is very readily soluble in ether, alcohol, and warm benzene, dissolves also in cold alkalis and alkaline carbonates, from which solutions it cannot be extracted by ether; the potassium-derivative forms long yellow needles, the silver compound a yellow precipitate.

A. K. M.

**Pyrrylene Dimethyl Diketone.** By G. CIAMICIAN and P. SILBER (*Ber.*, **18**, 1466–1468).—The authors have simplified the method of obtaining this compound (see also p. 808) by heating pyrroline (5 grams) with acetic anhydride (50 grams) at  $240$ – $260^\circ$  for about six hours. The product is treated with sodium carbonate to neutralise the excess of acid, and repeatedly extracted with boiling water. The filtrate deposits long yellow crystals of pyrrylene dimethyl diketone on cooling, and that remaining in solution is extracted with ether.

By the action of fuming nitric acid on pyrrole dimethyl diketone, a *mononitro-derivative*,  $\text{NO}_2 \cdot \text{C}_4\text{NH}_2(\text{COMe})_2$ , is obtained melting at  $149^\circ$ . By the oxidation of pyrrole dimethyl ketone with alkaline permanganate a compound is formed which is assumed to be either



A. K. M.

**New Lutidine.** By A. LADENBURG and C. F. ROTH (*Ber.*, **18**, 1590—1593).—A third lutidine is precipitated as hydrochloride on adding platinum chloride to the fraction of bone oil distilling at  $174$ — $176^\circ$ . The free base,  $\text{C}_7\text{H}_9\text{N}$ , boils at  $174$ — $176^\circ$ , and distils readily with steam; it is sparingly soluble in cold, still less in warm water, and is soluble in all proportions in ether, benzene, alcohol, and chloroform. Sp. gr. at  $0^\circ = 0.9861$  (water at  $4^\circ = 1$ ). Only a very minute quantity of an acid is formed on treatment with permanganate, the greater portion being completely oxidised. The hydrochloride and hydrobromide crystallise in long needles; the platinochloride,  $(\text{C}_7\text{H}_9\text{N})_2, \text{H}_2\text{PtCl}_6$ , forms short, bronze-coloured needles.

A comparison of the derivatives of the  $\alpha$ - $\gamma$ -lutidine described by the author (this vol., p. 815), and of the  $\alpha$ - $\gamma$ -lutidine described by Hantzsch (this vol., p. 397), has shown the identity of the substances.

A. J. G.

**Action of Ethyl Diacetosuccinate on Ammonia.** By L. KNORR (*Ber.*, **18**, 1558—1567).—In a former paper (this vol., p. 554) the author showed that the action of ethylic diacetosuccinate on ammonia and primary amines led to the formation of substances which, from their behaviour, he regarded as substituted pyrrolines, although none of them were identified with known pyrroline-derivatives; from one of these compounds he has now, however, obtained a dimethylpyrroline identical with that separated from animal tar.

*Ethylic dimethylpyrrolinedicarboxylate* melts at  $99^\circ$ , not at  $90$ — $91^\circ$ , as previously stated; it is readily soluble in alcohol and chloroform, sparingly soluble in ether, nearly insoluble in water, dilute acids, and alkalis, and has both acid and basic properties. The platinochloride,  $(\text{C}_{12}\text{H}_{17}\text{NO}_4)_2, \text{H}_2\text{PtCl}_6$ , forms orange-red crystals. The potassium-derivative,  $\text{C}_{12}\text{H}_{16}\text{KNO}_4$ , is obtained as a crystalline powder by the action of potassium or of solid potash on an ethereal solution of the salt.

*Hydrogen ethyl dimethylpyrrolinedicarboxylate*,



is obtained, together with the free acid, by boiling the diethyl salt with alcoholic potash, acidulating, &c. It forms slender crystals, and melts at  $227^\circ$  with decomposition into carbonic anhydride and ethyl-dimethylpyrrolinecarboxylate.

*Dimethylpyrrolinedicarboxylic acid*,  $\text{C}_4\text{NHMe}_2(\text{COOH})_2$ , crystallises in tufts of needles; it melts at  $251^\circ$  with decomposition into carbonic anhydride and dimethylpyrroline. When oxidised with potassium permanganate it yields pyrrolinetetracarboxylic acid. Many of its salts are described.

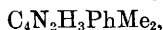
*Dimethylpyrrolinecarboxylic acid*,  $\text{C}_4\text{NH}_2\text{Me}_2 \cdot \text{COOH}$ , prepared by

saponification of its ethyl salt, closely resembles the dicarboxylic acid; it melts at 210—213° with decomposition into carbonic anhydride and dimethylpyrroline. The silver, lead, and iron salts are described. The *ethyl salt*,  $C_4NH_2Me_2 \cdot COOEt$ , prepared as above mentioned, crystallises in flat prisms, melts at 117—118°, boils at 290° under 731 mm. pressure, and distils readily with steam.

*Dimethylpyrroline*,  $C_4NH_3Me_2$  [Me : Me = 2 : 5], obtained by heating the mono- or di-carboxylic acids, forms a nearly colourless oil, which soon turns red on exposure to air, and is gradually converted into a red resin; it boils at 165° under 740 mm. pressure. In all its properties and reactions it shows complete identity with the dimethylpyrroline described by Ciamician and Weidel (Abstr., 1880, 404).

A. J. G.

**Action of Ethyl Diacetosuccinate on Phenylhydrazine.** By L. KNORR (*Ber.*, 18, 1568—1569).—*Phenyldimethylpyridazine*,



is prepared by heating phenyldimethylpyridazinedicarboxylic acid (this vol., p. 555) at 200°. It closely resembles paratolyldimethylpyrroline (*loc. cit.*) in properties, melts at 82°, boils at 176° under 730 mm. pressure, and distils readily with steam. It is insoluble in water and alkalis, soluble in concentrated acids, but is reprecipitated on dilution. It gives a deep cherry-red coloration with a solution of phenanthraquinone in acetic acid.

Hydroxylamine reacts with ethyl diacetosuccinate, forming a compound of the formula  $C_{12}H_{17}NO_5$ , from which a series of derivatives can be obtained differing from the pyrroline-derivatives described (*loc. cit.*) by containing 1 atom more oxygen. These substances are under investigation.

A. J. G.

**Caffeine.** By E. SCHMIDT and E. SCHILLING (*Annalen*, 228, 141—176).—In previous communications the authors have described caffeine methylhydroxide and some of its decomposition-products (Abstr., 1883, 872, and 1884, 335).—Caffeine is decomposed by boiling with baryta-water, yielding carbonic anhydride and caffeidine; the latter base is also decomposed by the continued action of the reagent, and it splits up into methylamine, sarcosine, formic acid, and carbonic anhydride. On boiling with baryta-water, caffeine methylhydroxide splits up directly into methylamine, sarcosine, formic acid, and carbonic anhydride. Neither caffeidine nor methylcaffeidine can be detected amongst the decomposition-products.

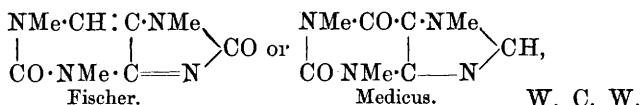
*Methylcaffuric acid*,  $C_7H_{11}N_3O_4$ , is prepared by boiling allocaffeine in water until the evolution of carbonic anhydride ceases. The substance crystallises in needles melting at 167°. It dissolves freely in water, alcohol, and chloroform. It is decomposed by basic lead acetate into mesoxalic acid, methylamine, and dimethylcarbamide.

In caffeinemethylhydroxide, the group  $CH_2 \cdot OH$  appears to be attached to that N-atom which is present in caffeine as an ammonia, not as a methylamine residue, since caffeinemethylhydroxide, unlike caffeine, yields on decomposition methylamine, and not ammonia.

It is not possible to decide from these experiments which of the



following formulæ represents the constitution of caffeine, but the authors are inclined to give the preference to Fischer's formula :—



**Papaverine.** By A. CLAUS and E. HÜETLIN (*Ber.*, **18**, 1576—1579).—The additive compounds of papaverine and the alkyl haloids are prepared by heating the components in sealed tubes in the water-bath for 6 to 7 hours in the case of the bromides, whilst 18—20 hours' heating is required for the iodides.

*Papaverine methiodide*,  $\text{C}_{21}\text{H}_{21}\text{NO}_4 \cdot \text{MeI}$ , crystallises in colourless plates, melts at  $80^\circ$  (uncorr.), and is readily soluble in chloroform, sparingly soluble in benzene, nearly insoluble in ether.

*Papaverine ethiodide*,  $\text{C}_{21}\text{H}_{21}\text{NO}_4 \cdot \text{EtI}$ , crystallises in short, pale-yellow granular crystals, and melts at  $216^\circ$ ; the solubilities resemble those of the methyl-compound. The *ethobromide*,  $\text{C}_{21}\text{H}_{21}\text{NO}_4 \cdot \text{EtBr}$ , crystallises in nodular aggregates of needles containing water of crystallisation, melts at  $110$ — $111^\circ$  (uncorr.), and is soluble in water and alcohol. The *ethochloride*,  $\text{C}_{21}\text{H}_{21}\text{NO}_4 \cdot \text{EtCl} + 4\text{H}_2\text{O}$ , prepared by the action of silver chloride on the bromide, crystallises in short colourless prisms. The *platinochloride*,  $(\text{C}_{21}\text{H}_{21}\text{NO}_4)_2 \cdot \text{Et}_2\text{PtCl}_6$ , forms a heavy yellow precipitate, and melts at  $223^\circ$  with decomposition. The *hydrozide* was obtained as an uncrystallisable brown mass. The *nitrate*,  $\text{C}_{21}\text{H}_{21}\text{NO}_4 \cdot \text{EtNO}_3 + 3\text{H}_2\text{O}$ , forms small prisms.

*Papaverine benzylchloride*,  $\text{C}_{21}\text{H}_{21}\text{NO}_4 \cdot \text{C}_7\text{H}_7\text{Cl} + 7\text{H}_2\text{O}$ , crystallises in large octahedrons. The *platinochloride*,  $(\text{C}_{21}\text{H}_{21}\text{NO}_4 \cdot \text{C}_7\text{H}_7)_2 \cdot \text{PtCl}_6$ , forms a yellow crystalline powder, nearly insoluble in water.

These additive compounds when boiled with potash are converted into substituted papaverines, which are still under investigation.

A. J. G.

**Narceine.** By A. CLAUS and C. RITZFELD (*Ber.*, **18**, 1569—1576). *Narceine ethobromide*,  $\text{C}_{23}\text{H}_{29}\text{NO}_9 \cdot \text{EtBr}$ , is prepared by the long contact of its components in the cold, or by heating the mixture for five hours at  $100^\circ$  in a reflux apparatus. It crystallises in slender white needles, melts at  $165^\circ$  (uncorr.), and is readily soluble in alcohol and hot water, less soluble in chloroform, insoluble in ether. The *cadmio-bromide*,  $\text{C}_{23}\text{H}_{29}\text{NO}_9 \cdot \text{EtCdBr}_2$ , crystallises in small colourless needles. *Narceine ethochloride* is prepared by the action of silver chloride on the bromide, it crystallises in small colourless needles, and melts at  $170^\circ$ . The *platinochloride*,  $(\text{C}_{23}\text{H}_{29}\text{NO}_9)_2 \cdot \text{Et}_2\text{PtCl}_6$ , forms lustrous yellow needles, and melts at  $170^\circ$  (uncorr.). The *mercurichloride*,  $\text{C}_{23}\text{H}_{29}\text{NO}_9 \cdot \text{EtHgCl}_3 + \text{H}_2\text{O}$ , forms a crystalline white precipitate, and melts at  $127^\circ$  (uncorr.). *Narceine ethyl nitrate*,  $\text{C}_{23}\text{H}_{29}\text{NO}_9 \cdot \text{EtNO}_3$ , crystallises in groups of long silky needles, melts at  $155^\circ$ , and is very soluble in cold water. The *ethyl oxalate*,  $(\text{C}_{23}\text{H}_{29}\text{NO}_9)_2 \cdot \text{Et}_2\text{C}_2\text{O}_4 + 6\text{H}_2\text{O}$ , crystallises in lustrous needles, and melts at  $174^\circ$  with decomposition.

*Narceine methiodide*,  $\text{C}_{23}\text{H}_{29}\text{NO}_9 \cdot \text{MeI}$ , is formed by heating a mixture of its components. It crystallises in very pale yellow, slender needles, melts at  $173^\circ$  with decomposition, and is readily soluble in water and

alcohol. The methochloride forms small white needles and melts at  $210^{\circ}$ . The platinochloride forms a clear yellow crystalline powder and melts at  $189^{\circ}$ . The *methyl nitrate*,  $C_{23}H_{29}NO_9$ ,  $MeNO_3$ , forms small white needles.

*Narceine benzyl chloride*,  $C_{23}H_{29}NO_9$ ,  $C_7H_7Cl$ , crystallises in slender white needles, melts at  $162^{\circ}$  (uncorr.), and is readily soluble in alcohol and hot water. The *platinochloride* forms a clear yellow, heavy crystalline powder and melts at  $165^{\circ}$ . The *hydroxide* is obtained as a viscid amorphous mass; the *carbonate* crystallises in white needles, and melts at  $135^{\circ}$ .

*Methylnarceine*,  $C_{23}H_{28}MeNO_9$ , is prepared by boiling narceine methiodide with aqueous potash. It crystallises in small colourless needles, melts at  $175^{\circ}$  (uncorr.), is sparingly soluble in water, chloroform, and benzene, readily soluble in alcohol, nearly insoluble in ether; the solutions have an alkaline reaction. Its salts form uncrystallisable resinous masses.

*Benzylnarceine*,  $C_{23}H_{28}(C_7H_7)NO_9$ , prepared by the action of aqueous potash on narceine benzyl chloride, crystallises in long white needles, melts at  $169^{\circ}$  (uncorr.), is nearly insoluble in water and ether, readily soluble in alcohol. Most of the salts do not crystallise. The platinochloride,  $[C_{23}H_{28}(C_7H_7)NO_9]_2$ ,  $H_2PtCl_6 + 2H_2O$ , forms a dark yellow crystalline powder, and melts at  $128^{\circ}$  (uncorr.).

When oxidised with potassium permanganate in acid solution, narceine yields a new base of the formula  $C_{17}H_{25}NO_{10}$ . A. J. G.

**Cupreine and Homoquinine.** By B. H. PAUL and A. J. COWNLEY (*Pharm. J. Trans.*, [3], 15, 729—731).—From recent observations the authors conclude that homoquinine consists of 39.08 per cent. quinine and 60.92 per cent. cupreine (compare this vol., p. 564).

D. A. L.

**Benzoylcegonine.** By W. MERCK (*Ber.*, 18, 1594).—*Benzoylcegonine*,  $C_9H_{14}NO_3Ez$ , is obtained as a bye-product in the preparation of cocaine. It crystallises in colourless, flat prisms, melts at  $188.5$ — $189^{\circ}$ , turning brown at the same time, and is readily soluble in water, more sparingly in alcohol, nearly insoluble in ether. When heated with hydrochloric acid at  $100^{\circ}$  it is resolved into benzoic acid and ecgonine.

A. J. G.

**Curarine from Strychnos Toxicifera.** By VILLIERS (*J. Pharm.*, [5], 11, 653—654).—The author has endeavoured to isolate the toxic principle from the root bark. The final product was found to be ordinary curarine. Attempts to isolate pure curarine were not successful.

J. T.

**Preparation of Hemialbumose from Vegetable Albumin.** By F. SZYMANSKI (*Ber.*, 18, 1371—1375).—Hemialbumose possessing the characteristic properties of the hemialbumose prepared from animal albumin, may be prepared from the vegetable albumin from barley, but it is obtained much more readily and in far larger quantity from conglutin from the yellow lupin. The vegetable albumin or conglutin is heated on the water-bath at  $98$ — $95^{\circ}$  with water containing 0.4 per

cent. sulphuric acid; as soon as a gelatinous mass is formed a large excess of the dilute acid is added, and the whole further digested at the same temperature until it becomes fluid, which happens in about three hours, any small quantity of turbidity is removed by filtration, and sodium hydroxide is added to the clear liquid until it is only very slightly acid, a precipitate is then slowly thrown down which consists almost entirely of hemialbumose, the solution still contains considerable quantities of hemialbumose in solution which may be partially precipitated by heating; this precipitate whilst fresh is soluble in hot water, but after treating with alcohol and drying over sulphuric acid it is no longer soluble. A very pure sample of hemialbumose was prepared by fractional precipitation, washing with a saturated solution of common salt, redissolving the precipitate in water, removing the salt by dialysis, precipitating the solution thus prepared with alcohol, washing the precipitate with alcohol and ether, and drying over sulphuric acid; thus obtained it was soluble with difficulty in cold water, but almost completely in hot, the greater part being reprecipitated on cooling. Acetic acid with sodium chloride or potassium ferrocyanide forms a precipitate in the aqueous solution which is dissolved on heating but reappears on cooling, dilute nitric acid also gives a precipitate which is dissolved on heating, and on adding an excess of nitric acid it is dissolved in the cold with an intense yellow colour. This sample contained 1.241 per cent. of ash.

A. P.

**Decomposition of Proteïds by Fermentation: Formation of Non-hydroxylated Aromatic Acids.** By E. SALKOWSKI (*Zeit. physiol. Chem.*, **9**, 491—510).—The results of the author's previous investigations (E. and H. Salkowski, *Abstr.*, 1879, 465 and 659; 1880, 413) are confirmed by the subsequent researches herein detailed.

Of the aromatic acids resulting from the fermentation of proteïds and separated in this way, phenylacetic or hydrocinnamic acid is invariably obtained, and frequently both. Their relative proportion is, however, variable. The following record of observations of the formation of the one or the other is given:—

Hydrocinnamic acid was obtained in—(1.) 9 experiments with meat, duration of fermentation 2—16 days. (2.) 2 experiments with blood fibrin, duration of fermentation 3—7 days. (3.) 1 experiment with meat fibrin, duration of fermentation 13 days. (4.) 1 experiment with pancreas peptone, duration of fermentation 7 days.

Phenylacetic acid was obtained in—(1.) 3 experiments with serum albumin, duration of fermentation 37—39 days. (2.) 2 experiments with meat, duration of fermentation 7—14 days.

In the case of one experiment with meat both acids were isolated.

The difficulty of separating these acids from one another was overcome by the expedient of their physiological transformation (through the digestive apparatus of the rabbit) into hippuric and phenaceturic acids respectively (*comp. ibid.*, **7**, 161). Their isolation from the

urine and subsequent separation was carried out quantitatively with the following results :—

Substance fermented.	Duration of fermentation.	Albuminoid dissolved.	Hippuric acid.	Phenaceturic acid.
Fibrin . . . .	4	452 grams	6·088	0
„ . . . .	9	1974 „	30·894	2·233
„ . . . .	13	387 „	6·375	0·175
„ . . . .	22	402 „	7·160	traces
„ . . . .	26	498 „	6·272	0·255
„ . . . .	38	488 „	5·722	0·427
Meat . . . . .	11	370 „	8·266	0·932
Pancreas } peptone }	12	1059 „	12·933	2·808

In conclusion, the author discusses the probable sources of the volatile aromatic acids, and the views which have been expressed thereon, pointing to tyrosine on the one hand, and the preformed phenyl amido-acid-groups contained in the molecule of the proteïds on the other (comp. Nencki and Sieber, *Ber.*, **18**, 394), summing up the evidence in favour of the latter.

C. F. C.

## Physiological Chemistry.

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**Assimilation (Reabsorption) of Fat.** H. A. LANDWEHR (*Zeit. physiol. Chem.*, 9, 361—379).

**Influence of Bile, Bile Salts, and Bile Acids on Amylolytic and Proteolytic Action.** By R. H. CHITTENDEN and G. W. CUMMINS (*Amer. Chem. J.*, 7, 36—52).—In the first series of experiments the ferment used was a filtered and neutralised solution of saliva, and was allowed to act on a 1 per cent. starch solution for 30 minutes at 40°; the dextrose (and maltose) formed were estimated gravimetrically. The following results were obtained:—

Addition of *free* taurocholic or glycocholic acid (0·1 and 0·2 per cent. respectively) reduces the action to one-tenth. No marked effect is produced by addition of 0·5 per cent. sodium glycocholate, but the same quantity of sodium taurocholate reduces the action to one-thirtieth. Fresh ox-bile may be added to the extent of 20 per cent. without influencing the action, and it is therefore probable that the retarding action of the bile acids is counterbalanced by the presence of some other substance in the bile; the slight diastatic power of bile is not sufficient to account for the inactivity of the bile.

In the second series an extract of pig's stomach was allowed to act on blood fibrin; the insoluble fibrin was estimated. Addition of

taurocholic acid and its sodium salt have a powerful retarding action; glycocholic acid and its salts on the other hand have none; more than 1 per cent. of bile also retards the action, and 20 per cent. stops it; hence the reflux of but a small quantity of bile into the stomach would be attended with decreased proteolytic action.

The proteolytic action of trypsin in neutral solution is increased by addition of 0.1 to 0.5 per cent. sodium carbonate, but further additions rapidly decrease the action. Combined salicylic acid has a great reducing power, and free salicylic acid stops the action completely; hydrochloric acid acts even more energetically. In an ordinary digestive mixture, or even when albuminous matter is present only in limited quantity, the addition of hydrochloric or salicylic acid to a neutral solution containing trypsin reduces its proteolytic action to a minimum before any free acid is present. The addition of bile, of sodium glycocholate, or taurocholate produces scarcely any retarding action, but free taurocholic acid exerts a marked influence.

H. B.

**The Proteïds of Cow's Milk.** By J. SEBELIEN (*Zeit. physiol. Chem.*, 9, 445—464).—The author has isolated from milk two albuminoid substances distinct from casein.

*Lactoglobulin*, the first of these, is present in minute quantity only. To obtain this substance the casein is first thrown down by means of common salt, and the globulin in the filtrate precipitated by saturating with magnesium sulphate. After careful purification it was found to be homogeneous and of uniform properties, exhibiting the closest resemblance to the paraglobulin of blood.

*Lactalbumin*, the second albuminoid, is precipitated by acetic acid in the filtrate from the preceding compound. After purification it was analysed, with the following results, calculated on the ash-free substance (ash = 1.13 per cent.) :—

C.	H.	N.	S.	P.
52.19	7.18	15.77	1.73	0.18

Its properties are closely similar to those of serum albumin, but differ in the one important particular that its specific rotation  $[\alpha]_D = 36.6^\circ$ , whereas that of serum albumin is  $62^\circ$ . This difference in optical properties was established beyond doubt by various confirmatory observations.

C. F. C.

**Milking of Cows.** By M. SCHMÖGER (*Bied. Centr.*, 1885, 331).—To estimate the advantage of milking three times a-day over twice a-day, two cows were submitted to the experiment, when it was evident that much more milk was obtained by thrice milking; moreover, as the milk was no poorer in fat, there was consequently a larger total yield of butter.

E. W. P.

**Chemical Changes attending the Development of the Embryo in the Eggs of the Bombyx Mori.** By A. TICHOMIROFF (*Zeit. physiol. Chem.*, 9, 518—532).—The fertilised eggs of this insect

undergo a developmental differentiation during the summer, accompanied by a change in colour from yellow to violet. This is due to a formation of pigment in the embryonal envelope. During the winter all changes are suspended. The eggs were first examined after the expiration of this quiescent period. They are composed of a yolk, yolk envelope, and chorion. These have been analysed by the author, the two former together as they are not separable. The chorion was isolated by alternate treatment with dilute acid and pepsin solution. Several preparations were analysed with concordant results, from which, together with the freedom of this substance from chitin, the author infers that it is chemically homogeneous, and designates it by the term *chorionin*. Its empirical composition is as follows:—

C.	H.	N.	S.	O.	Ash.
47.27	6.71	16.93	3.67	24.72	0.70

During the process of hatching the total loss in weight was 11.16 per cent., and the changes in composition (yolk) are expressed by the comparison of the percentages of the constituents of the eggs at the beginning (A) and at the end (B) of this period, which are as follows:—

	A.	B.
Aggregate substance .....	100.00	88.84
Dry matter .....	35.51	30.20
Albumin and insoluble salts .....	11.31	9.20
Aqueous extract .....	5.81	5.46
"          containing glycogen ...	1.98	0.74
Ethereal extract .....	9.52	6.46
"          containing fat .....	8.08	4.37
"          "          lecithin ....	1.04	1.74
"          "          cholesterin..	0.40	0.35
Chorionin .....	8.87	(8.87)
Chitin .....	—	0.21
Organic bases .....	0.02	0.21

The following statistics are given of the loss of weight sustained during the process of hatching, which the author finds to be proportional to the morphological differentiation:—

Days.	Absolute weight.	Daily loss.	Days.	Absolute weight.	Daily loss.
—	1.0388	—	—	0.6854	—
8	1.0029	$\frac{0.0359}{7}$	3	0.6776	$\frac{0.0078}{3}$
9	0.9952	0.0077	4	0.6739	0.0037
11	0.9624	$\frac{0.0328}{2}$	5	0.6687	0.0052
12	0.9428	0.0196	6	0.6562	0.0125
13	0.9229	0.0199	7	0.6490	0.0072
			8	0.6328	0.0162
			9	0.6152	0.0176

C. F. C.

**Physiological Action of Potassium Chlorate.** By J. v. MERING (*Chem. Centr.*, 1885, 249).—The author confirms Marchand's view that this salt converts the hæmoglobin in the blood into metahæmoglobin, thus rendering the blood useless for the process of respiration. This action is dependent on the amount of chloric acid present, which has just the same effect as the salt. J. K. C.

**Physiological Action of the Tertiary Alcohols.** By H. THIERFELDER and J. v. MERING (*Zeit. physiol. Chem.*, 9, 511—517).—Tertiary butyl alcohol introduced into the stomach of the rabbit was found to have a slightly narcotic action when the quantity exhibited amounted to 6 c.c. Tertiary amyl alcohol exerted a much more powerful action, a dose of 3 c.c. causing, in a few minutes, a deep sleep lasting 12—24 hours; on waking the animal showed no morbid symptoms. The lethal dose for dogs of medium size was from 10 to 20 c.c. The recovery from the effects of smaller doses was complete. Tertiary hexyleneglycol (pinacone) was next investigated; its action was also narcotic, but less powerful than that of the preceding compounds. These compounds were found in the urine in combination with glycuronic acid; and were isolated in the form of the potassium salts of the conjugated acids. These were analysed, and a portion also treated with boiling dilute sulphuric acid, by which they were resolved into glycuronic acid and the respective alcohols.

C. F. C.

**Action of Cocaine on the Invertebrates.** By RICHARD (*Compt. rend.*, 100, 1409—1411).

**Formation and Migration of Fat in Phosphorus Poisoning.** By H. LEO (*Zeit. physiol. Chem.*, 9, 469—490).

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## Chemistry of Vegetable Physiology and Agriculture.

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**Influence of Oxygen on Fermentation.** By E. BUCHNER (*Zeit. physiol. Chem.*, **9**, 380—415).—The author in the first instance exhaustively criticises the experimental method of the investigation, as well as the deductions therefrom, which led Pasteur to the enunciation of his well-known theory of anærobic fermentation. The ratio of yeast development, that is the number of cells to the sugar fermented, which Pasteur adopted as the measure of “le pouvoir du ferment,” is a misleading expression, and by introducing into it the factor of time, which is obviously necessary, and calculating for  $\frac{y}{z \cdot t}$  instead of  $\frac{y}{z}$ , his results by no means favour the theory in question. In regard to schizomycetic fermentation the evidence as to loss of fermentative activity, with diminished movement of the organisms, is assumed by Pasteur, but denied by the author on the basis of his own experiments with pure

cultivations of the butyl bacillus. In reviewing the literature of the subject, and chiefly the contributions of Schützenberger, Nägeli, and Hoppe-Seyler, the author concludes that exact experiments have been made in regard to yeast only, the result of which has been to modify very considerably the theory of Pasteur. The author experimented with the three organisms:—(1) *Bacterium Fitz*, (2) *Butyl bacillus*, (3) *Bacillus subtilis*. Of these pure growths were cultivated. The solution used in the experiments contained 2·5 per cent. of glycerol, 0·25 meat extract, with 5 per cent. calcium carbonate also added. The experiments were conducted in three parallel series, in which the conditions were uniform in all respects save the one to be investigated, namely, the gas environment, which was so varied that in A a stream of oxygen was maintained throughout the fermentation period, in B a stream of hydrogen, whilst in C the normal atmospheric conditions obtained.

The following conclusions are warranted by the experiments. The quantity of glycerol fermented, as well as the numerical increase of the organisms, is greater in presence of oxygen. The ratio of the quantity of carbonic anhydride formed to glycerol fermented remains the same when oxygen is replaced by an inert gas.

At the same time the numerical increase of the organisms is so much greater in the case of the oxygen, that when divided into the number expressing the chemical results of the fermentation, which gives an expression for the fermentative activity of the individual organism, this is seen to be less than in the case of hydrogen or atmospheric air. For the details of the investigation, which are important, the original must be consulted.

C. F. C.

**Selective Alcoholic Fermentation.** By E. BOURQUELOT (*Comp. rend.*, 100, 1404—1406 and 1466—1469).—Dubrunfaut has supposed that a ferment such as yeast when introduced into a mixture of several fermentable sugars has the power of selecting some particular sugar, which it attacks and destroys before the others are affected, and the fact that the lœvorotatory power of invert-sugar undergoing fermentation does not continually diminish, as it would do if the two sugars were destroyed with equal rapidity, has been taken to support this view.

The author finds, however, that when yeast is introduced into a mixture of maltose and levulose or of glucose and levulose, both sugars ferment simultaneously, but at unequal rates. In the first mixture the levulose ferments more rapidly than the maltose, whilst in the second the glucose ferments more rapidly than the levulose. In both cases, however, at a certain stage in the fermentative process, the order of selection, or the relative rate of fermentation, becomes reversed.

Experiments were made with a view to ascertain how far the observed results were due to an actual selective power possessed by the ferment, and how far to the various conditions, such as temperature, dilution, &c.

It was found that in a mixture of equal parts of maltose and evulose the destruction of levulose by yeast increases more rapidly

with the concentration of the solution than does the destruction of maltose, whilst if the liquid is diluted the rate of destruction of the levulose diminishes more rapidly than that of the maltose. The presence of alcohol has the same effect as dilution.

In the process of fermentation it is probable that the dissolved sugars undergo no change until they have penetrated through the cellular membrane of the ferment and come into contact with the protoplasm in the cells. If any true selective fermentation takes place it may depend on the relative rapidities with which the different sugars penetrate the cellular membrane, or it may be due to some action in the interior of the cell.

The author finds that when a mixture containing 2 per cent. of maltose and 2 per cent. of levulose is dialysed through parchment paper, the levulose passes through more rapidly than the maltose, but with a solution containing 2 per cent. of maltose and only 1 per cent. of levulose the rate of dialysis is reversed. The presence of alcohol diminishes the absolute rate of dialysis but does not affect the relative rates, and an increase of temperature accelerates dialysis but does not alter the relative rapidities. The effect of alcohol and of temperature differentiates dialysis from the so-called selective fermentation.

Experiments were made to ascertain the relative rates of fermentation of separate solutions (2 per cent.) of glucose and levulose under precisely similar conditions. It was found that glucose ferments more quickly than levulose, and that dilution, presence of alcohol, &c., have the same effect on the sugars separately as when they are mixed.

From these results it follows that there is no real selective fermentation, but that in a mixture of sugars each constituent ferments according to its own peculiar laws, independently of the other constituents.

C. H. B.

**Fate of Sulphur in Germination.** By G. TAMMANN (*Zeit. physiol. Chem.*, 9, 416—419).—The specimen of peas, the germination of which was studied by the author, contained 0.143 per cent. total sulphur, of which  $0.027 = 0.07 \text{ SO}_3$  was in the form of soluble sulphates. The sulphuric acid was determined during the early periods of growth with the following results:—

Days . . . . .	5	10	15	20	25
SO <sub>3</sub> per cent..	0.089	0.172	0.160	0.173	0.191

In the above the germination and growth took place in the dark; similar results were obtained in the light. The phosphoric acid similarly underwent increase, from 0.324 per cent. P<sub>2</sub>O<sub>5</sub> in the original seed, to 0.443 per cent. after germination, followed by 12 days' growth in the dark. These results are in opposition to those obtained by O. Kellner (this Journal, 1875, 777).

C. F. C.

**Formation of Starch in Vine Leaves.** By G. CUBONI (*Ann. Agronom.*, 11, 236—239).—The method and general results of this investigation have already appeared in this Journal (this vol., p. 683).

The starch observed in the leaf at any time is only the excess of that produced over that which disappears. The author has not succeeded in demonstrating the transformation into sucrose or glucose of the starch granules which disappear: some experiments even negative this hypothesis, and it is suggested that tannin is the product of transformation. Is this metamorphosis of the starch due to a diastatic ferment, or has the green cell itself the power of effecting it? If an annular incision be made through the soft portion of the stem above and below the insertion of a leaf, the starch already formed in the leaf will no longer disappear in the dark, but with one incision only, either above or below the leaf, the starch disappears as usual. When a grape-cluster, either in flower or fruit, is opposite the leaf the starch disappears in the dark, even when the stem is cut through above and below. It appears from this that the metamorphosis of the starch is due neither to a special ferment nor to the cell activity of the leaf, but is only brought about by a demand for fresh supplies of carbohydrates in some centre of growth.

J. M. H. M.

**Acquisition of Atmospheric Nitrogen by Plants.** By W. O. ATWATER (*Amer. Chem. J.*, 6, 365—388).—Doubting the correctness of the generally received view that plants do not assimilate nitrogen from the atmosphere, the author has made experiments on this subject. Peas were grown in sand which had been purified by igniting and washing. The plants were nourished by solutions containing known quantities of nitrogen. The amounts of nitrogen in the seed and in the nutritive solutions supplied were compared with those found at the end of the experiments in the residual solution (obtained by washing the sand) and in the plants. The excess of the latter over the former—in some cases very large—must represent nitrogen absorbed from the atmosphere. The conditions of growth were varied as follows:—1. By varying the concentration of the nutritive solution from 0·8 to 5 or 6 parts by weight of dissolved salts in 1000 of solution (1 part in 1000 has been found most favourable to normal growth). 2. By varying the total quantity of food supplied to the roots by the solutions, from an amount seemingly sufficient, or nearly so, for normal growth, to a very scanty supply. 3. By varying the proportion of nitrogen in the solution, making it in some cases rather, in others very small, compared with the amount of mineral food, so that the plants were enabled to make some growth at the expense of the nitrogen furnished to the roots, and left to gather the rest of their nitrogen, if possible, from the air. The solutions used contained mixtures of the following salts: potassium and calcium nitrates, magnesium sulphate, potassium phosphate, and ferric chloride. The plants were grown in pots in the open air, but protected from dew and rain by being put under cover at night and in rainy weather. The following table gives the nitrogen statistics obtained. The experiments A, B, C were preliminary ones. In the others the seeds were planted on March 30th, and the plants harvested on July 3rd; but as they were ripe, and watering ceased, some time before the latter date, the actual time of growth should be taken at about 72 days. One-third of the pots had 1 kilo. sand each, one-third 2 kilos., and

one-third 3 kilos., so that as they were kept saturated (or nearly so) with pure water, the concentration of the solutions differed widely. The solutions in the 3 kilo. pots contained from 0·8—1·6 grams salts in 1000 c.c. water, and were consequently favourable to the growth of the plants; those in the 1 and 2 kilo. pots contained from 2·5—6 parts per 1000, and were therefore unfavourable to growth. One-half of the pots contained three, the remainder six plants each. The amount of food was estimated to be rather small for three plants, and therefore very scanty for six, and therefore Nos. 3, 4, 7, 8, 11, and 12 were very insufficiently nourished. The amounts of mineral food was the same for all; the larger nitrogen ratio (136·9 mgrms.) supplied was calculated to be rather small in proportion to the mineral food.

No. of experiment.	Nitrogen supplied at the beginning and during the experiment.			Nitrogen found at end of the experiment.			Gain or loss of nitrogen.
	In seeds.	In solutions.	Total.	In vines, roots, &c.	In residual solutions.	Total.	
	mgrms.	mgrms.	mgrms.	mgrms.	mgrms.	mgrms.	mgrms.
A .....	49·5	61·4	110·9	167·2	7·2	174·4	+ 63·5
B .....	36·4	92·2	128·6	133·8	8·0	141·8	+ 13·2
C .....	35·6	61·4	97·0	108·7	1·3	110·0	+ 13·0
1 .....	36·7	59·4	96·1	116·4	1·4	117·8	+ 21·7
3 .....	72·6	59·4	132·0	158·9	3·8	162·7	+ 30·7
5 .....	34·2	59·4	93·6	156·1	0·0	156·1	+ 62·5
7 .....	71·5	59·4	130·9	158·1	0·0	158·1	+ 27·2
9 .....	35·3	59·4	94·7	186·5	1·4	187·9	+ 93·2
11 .....	72·5	59·4	131·9	210·9	2·7	213·6	+ 81·7
2 .....	34·4	136·9	171·3	178·9	2·0	180·9	+ 9·6
4 .....	75·2	136·9	212·1	200·6	12·8	213·4	+ 1·3
6 .....	34·8	136·9	171·7	149·6	1·2	150·8	- 20·9
8 .....	70·3	136·9	207·2	197·5	12·7	210·2	+ 3·0
10 .....	34·6	136·9	171·5	277·8	35·7	313·5	+ 142·0
12 .....	68·8	136·9	205·7	260·2	45·7	305·9	+ 100·0

These results seem to leave no doubt that the plants had in some way abstracted nitrogen from the surrounding air. *In the four experiments with sufficiently dilute solutions for normal growth the poorly-fed plants obtained one-third, those tolerably well-fed, one-half of their whole nitrogen from the atmosphere.* In the other cases the gain was less, but still, with one exception, very marked. The author is unable to explain this one exception, unless it be by the decomposition of nitrates in the presence of germinating seeds (as shown by Bous-singault), and in this case it is probable that more or less loss from this cause occurred in the other experiments. This and all other probable sources of error would tend to reduce the final total nitrogen,

and would also tend to show a still larger acquisition of atmospheric nitrogen than that actually proved to have taken place.

The amounts of nitrogen acquired by the plants were so large, that it is impossible that it can have been derived from ammonia, &c., dissolved out of the air by the moisture of the sand; since Heinrich's and Schlösing's experiments show that under the most favourable circumstances (absorption by dilute acid, &c.) not more than 9.8 mgrms. ammonia could have been so absorbed during the duration of the experiments.

The author considers these results as proving that *free* nitrogen is assimilated from the atmosphere by *healthy* growing plants. He thinks that the opposite results obtained by Boussingault, and by Lawes, Gilbert, and Pugh (*Phil. Trans.*, 1861, 2, 437) were possibly due to—i, the fact that their plants were grown under glass covers connected with the earth, and were therefore removed from the influence of the electricity of low potential which obtains in the strata of air near the earth, in which our plants grow; and ii, their plants being allowed exceedingly little combined nitrogen in their nutritive solutions. For, firstly, Berthelot has shown that free nitrogen may be assimilated by vegetable substances (such as dextrin, cellulose, &c.) under the influence of electricity of low potential—and it seems not improbable, therefore, that atmospheric electricity may play a similar part towards growing plants;—and, secondly, the author's experiments show that a deprivation of sufficient nitrogenous nourishment at once reduces the amount of external nitrogen assimilated.

L. T. T.

**Allantoin, Asparagine, Hypoxanthine, and Guanine as Plant-constituents.** By E. SCHULZE and E. BOSSHARD (*Zeit. physiol. Chem.*, 9, 420—444).—In continuation of previous researches on this subject (Abstr., 1881, 1061; 1882, 1195), the authors have devised an improved method, whereby they have succeeded in isolating 0.25 gram allantoin from 440 grams of the fresh young leaves of the plant. Previously they had obtained sufficient for mere identification only. No asparagine was present in the extracts.

The main feature of the improved method consists in precipitating these nitrogenous compounds by mercuric nitrate in the aqueous extract previously freed from the compounds precipitable by lead acetate. From the leaf-buds of *Acer pseudoplatanus* and *Acer campestre*, both allantoin and asparagine were isolated. From 1 kilo. of the former (= 170 grams dry substance) the quantities obtained were 0.5 gram allantoin and 5 grams asparagine. The leaf-buds of *Betula alba*, *Fagus silvatica*, *Populus nigra*, *Tilia parvifolia*, and *Vitis vinifera* were found to contain no allantoin, but asparagine in some quantity. Certain barks were next examined, stripped for the purpose from the younger branches, towards the end of October. Allantoin was found to be present in the bark of *Æsculus hippocastanum* and of *Acer pseudoplatanus*. Etiolated lupin plants in the early stages of growth, which contain asparagine and other products of resolution of proteids in large quantity, were found not to contain any allantoin.

Of fodder plants, grass, oats, and red clover were examined in the

early stages of growth, and found not to contain allantoin; moreover, from one only of these was asparagine isolated, 1 kilo. of the red clover yielding 0.25 gram. The quantity of the latter was considerably increased by keeping the plants for a week in the dark, with the lower end of the stem immersed in water; from 800 grams clover, after this treatment, 1.7 gram asparagine was obtained. A more remarkable result was obtained with oat plants, which yielded, after this treatment, 3.1 grams asparagine on 900 grams of substance (= 170 grams, anhydrous). In order to correlate this formation of asparagine with the presumed loss of proteids, the following determinations were made by Stutzer's method on the dry substance.

a. Freshly gathered. b. After 6—8 days in water:—

	Red clover.		Oats.	
	(a.)	(b.)	(a.)	(b.)
Total nitrogen ....	4.11	4.37	4.12	4.50
Proteid „ ....	3.22	2.47	3.51	1.46
Amide „ ....	0.89	1.90	0.61	3.04

Determinations by Sachsse's method gave confirmatory results. The authors incline to Borodin's view that amides are aggregated under these conditions by reason of the absence of such products, as under the condition of normal assimilation effect their reincorporation into proteid molecules.

The method of precipitation by mercuric nitrate, by which the authors find that hypoxanthine, xanthine, and guanine may also be more easily isolated, has enabled them to identify these bases in young potatoes (tubers), in sugar-beet, in the leaf-buds of the plane and maple, in the bark of the plane (branches), in lupins, and in young grass, red clover, oats, and vetch.

Details are also given of the isolation of these compounds, in particular cases, in quantity sufficient for a more complete identification of the individual bases.

The authors are not unmindful of the probability of the formation of these bases during the process of extraction, which point is discussed from time to time.

C. F. C.

**Chemical and Toxicological Relations of certain Fungi.** By R. BÖHM (*Chem. Centr.* [3], 16, 249—251).—*Boletus luridus* belongs to the class of not very poisonous fungi, and its composition varies in different seasons. It contains large quantities of choline together with a body similar to cholesterin, small quantities of muscarin, and an acid (luridic acid) crystallising in brilliant red needles, and yielding succinic acid on distillation. *Ananita pantherina* contains essentially the same substances, but its acid crystallises in yellow crusts.

J. K. C.

**Absorptive and Evaporative Powers of Various Litters.** By E. WOLLNY (*Bied. Centr.*, 1885, 305—309).

**Cultivation of Varieties of Oats.** By O. BESELER and M. MÄCKER (*Bied. Centr.*, 1885, 332—337).—The varieties of oats under

examination were nearly all foreign, and a great difference is observable in the yields, both of straw and grain, and also in the composition of the grain. The tables of analysis show that, as a rule, the heaviest cropper is the richest in albuminoids. The authors found that the straws of the kinds of oats he examined were poorer in albuminoids than is stated by Wolff and Kühn, who gave the mean quantity 4.0 per cent., whilst those under observation contained only 0.9—1.8 per cent.; there was not much variety of composition found in the chaff.

E. W. P.

**Keeping of Topped and Untopped Beet.** By J. HANAMANN (*Bied. Centr.*, 1885, 341—343).—Up to the end of January it appears to matter little whether the roots are topped or not, for they keep just as well either way; but after that time up to May the value of the untopped roots diminishes, and growth commences early at the cost of the juice, whilst the topped roots show no signs of growth, consequently the reduction in the percentage of sugar is less.

E. W. P.

**Arsenic in the Soil of Cemeteries.** By SCHLAGDENHAUFFEN and GARNIER (*Compt. rend.*, 100, 1388—1389).—Arsenic is found disseminated in variable but often considerable quantity in many soils in the Vosges, especially in red sandy soils, in which it probably exists as ferric arsenate. Ferric arsenate is slightly soluble in boiling water, but is quite insoluble in cold water, and cannot be extracted by rain water percolating through the soil.

When any compound of arsenic in aqueous solution is left in contact with an argilo-calcareous or argilo-ferruginous soil at the ordinary temperature, the arsenic is gradually converted into insoluble compounds, which are retained by the soil.

Any arsenical compound introduced into an argilo-calcareous or argilo-ferruginous soil, and subjected to continual infiltration of rain, if originally insoluble remains insoluble, but if soluble it gradually becomes insoluble, and at a depth of 0.6—0.9 m. from the point at which the arsenic is introduced, no arsenic can be detected in the infiltrated water, even after 14 months.

These results confirm those obtained by Orfila in 1847, and prove that arsenic cannot be transferred from an arsenical soil to a corpse through the medium of rain water percolating through the soil.

C. H. B.

**Manuring with Peat.** By WAGNER (*Bied. Centr.*, 1885, 352).—Peat compared with straw as a manure was found to be the more valuable; during two seasons it brought the highest crop of potatoes. With barley, however, the results were alike.

E. W. P.

**Action of Various Forms of Phosphoric Acid.** By FITTBOGEN (*Bied. Centr.*, 1885, 313—318).—Barley was grown in pots, mono-calcium, dicalcium phosphate, &c., being added to the soil in the pots. It appears that the phosphates most rapid in their action are mono- and di-calcium phosphate, precipitated phosphate, and good superphosphate from guano, &c. The phosphates of medium action are tricalcium phosphate as steamed bones, superphosphate from Lahn



phosphorite, and the like minerals. The slowest in their action are ferric, aluminic, and Kladno phosphates. These last phosphates are greatly assisted in their action by the presence of humic acid, either free or in combination. Field experiments corroborated the result obtained by pot culture, that precipitated phosphate is not far behind a high super in its action.

E. W. P.

**Manuring Experiments.** By J. KÖNIG (*Bied. Centr.*, 1883, 319—320).—These experiments were conducted on lupine-sick soil manured with kainite, phosphate and horn-meal, the crop being rye. The results, though not very satisfactory, show that the action of kainite applied in autumn is beneficial, and the addition of phosphates and nitrogen is productive of increased yield only when kainite is present. Kainite and nitre is better for potatoes than kainite and horn- or bone-meal. Some experiments show that where nitrate is used there are more diseased potatoes than on other plots.

E. W. P.

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## Analytical Chemistry.

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**Apparatus for the Correct Reading of Gas Volumes over Water.** By H. N. MORSE (*Amer. Chem. J.*, 7, 58—60).

**Precipitation of Halogen Salts of Silver.** By R. SCHNEIDER (*J. pr. Chem.* [2], 31, 420—428).—In the course of investigations on the atomic weight of antimony, it has been suggested that if a halogen salt of silver be precipitated from a solution containing antimonious oxide and tartaric acid, the precipitate is apt to retain small quantities of silver tartrate. In the case of a very strong solution, Cooke observed the presence of silver tartrate in a precipitate of silver chloride. In this paper this point is examined, and it is shown by various methods of investigation, that with proper precautions the precipitated halogen salt of silver does not retain recognisable quantities of silver tartrate, a result confirmed by Cooke's observations on the solubility of this salt. V. H. V.

**Schulze's Process for the Quantitative Determination of the Halogens in Aromatic Compounds.** By L. P. KINNICUTT and R. C. SWEETSER (*Amer. Chem. J.*, 6, 415—416).—The authors find that the use of this process (Abstr., 1884, 1422) is limited, many substances (such as ethyl phenyldibromopropionate) only giving up part (in the case cited half) of the halogen contained. L. T. T.

**Reactions for Distinguishing Chlorides, Bromides, and Iodides when mixed together.** By H. HAGER (*Chem. Centr.* [3],

16, 315).—A small portion of the salt to be tested is dissolved in a few c.c. of dilute sulphuric acid, and coloured with permanganate solution. With pure sodium chloride the colour disappears completely after a time, but if a trace of bromide be present the liquid becomes bright yellow, whilst a trace of an iodide turns it dark yellow. To test sodium bromide for iodine, dissolve in water, and tint with permanganate; the latter will turn brown in a few seconds if iodine is present.

J. K. C.

**Titration of Potassium Iodide.** By P. CARLES (*J. Pharm.* [5], 11, 504—506).

**Titration of Potassium Iodide.** By E. FALIÈRES (*J. Pharm.* [5], 11, 657—662).—The iodide is gradually heated up to 100° with a solution of ferric chloride, by which all the iodine is expelled, and is collected in an excess of standard sodium thiosulphate mixed with a few c.c. of chloroform. The excess of thiosulphate is then determined by standard iodine solution.

Bromides do not affect this modification of Deflos' method, whilst Berthet's process is influenced by them.

The author proposes the same reactions for the estimation of iron.

J. T.

**Volumetric Estimation of Nitrogen.** By F. HUFSCHMIDT (*Ber.*, 18, 1441—1444).—The author finds that in Dumas's method it is impossible to expel the whole of the air contained in the tube, blank experiments with hydrogen sodium carbonate yielding gas unabsorbable by potash as long as carbonic anhydride was evolved. When a separate apparatus is employed in which the carbonic anhydride is prepared by acting on a boiling solution of sodium carbonate with sulphuric acid, the gas obtained is also found to be incompletely absorbed by potash. Better results are obtained by the employment of marble and hydrochloric acid which is kept heated at nearly its boiling point; 3 litres of the gas so obtained only yielded 0.2 c.c. residue after absorption by potash.

The copper oxide should be strongly ignited in a current of carbonic anhydride, which is also passed as the oxide cools. The author allows an hour for a combustion, during which time about 3 litres of carbonic anhydride are used; 0.2 c.c. is therefore to be deducted from the total gas volume obtained. The measuring apparatus is a modification of Zulkowsky's.

A. K. M.

**Estimation of Nitrogen in Substances containing Organic, Ammoniacal, and Nitric Nitrogen.** By A. HOUZEAU (*Compt. rend.*, 100, 1445—1447).—50 grams of sodium acetate and 50 grams of sodium thiosulphate are fused together in their water of crystallisation, allowed to cool, and the mixture finely powdered and kept in a well-stoppered bottle; 2 grams of this mixture, with an equal weight of granular soda-lime, is introduced into the combustion tube, and the latter filled for a few centimetres with soda-lime; 0.5 gram of the substance to be analysed is *intimately* mixed with 10—15 grams of the mixed salts, and afterwards with 10 grams of finely powdered

soda-lime, and introduced into the combustion tube, which is then filled up with soda-lime in the usual way. The tube is carefully heated from front to back, and the evolved ammonia is collected in standard acid, or the exit tube may be allowed to dip into a vessel containing water, without appreciable loss. The saline mixture at the back of the tube replaces the oxalic acid which is usually employed, and will give off about 200 c.c. of gas. C. H. B.

**Qualitative Determination of the Bases without Hydrogen Sulphide.** By G. S. EYSTER (*Amer. Chem. J.*, **7**, 21—26).

**Gallein as an Indicator.** By M. DECHAN (*Pharm. J. Trans.* [3], **15**, 849—850).—The author finds gallein (pyrogallol-phthalein) more delicate and capable of more general application as an indicator than either phenolphthalein, litmus, or methyl-orange. D. A. L.

**Spectroscopic Determination of Lithium.** By L. BELL (*Amer. Chem. J.*, **7**, 35—36).—A standard solution of a lithium salt is diluted until a drop on a small loop of platinum wire only just shows the lithium line. The substance to be tested is treated in exactly the same way, and the amount calculated from the dilution by a simple proportion. The same platinum wire and flame are used in both cases. Very fair results are obtained. The method is especially suitable for the determination of lithium in mica, &c. H. B.

**Determination of the Value of Zinc-dust.** By H. N. MORSE (*Amer. Chem. J.*, **7**, 52—57).—Description of an apparatus for solution of the sample and determination of the hydrogen evolved. H. B.

**Separation of Copper and Cadmium.** By A. BÉHAL (*J. Pharm.* [5], **11**, 553—554).—When a strongly alkaline solution of sodium tartrate is added to a mixture of copper and cadmium salts, a clear liquid is obtained, especially after agitation. If now the solution be heated to boiling, the cadmium is completely precipitated as hydroxide, whilst the copper remains in solution. The precipitate rapidly settles, and after being filtered off, is washed with a few drops of water. After dissolving it in ammonia, ammonium sulphide gives a pure yellow precipitate.

Ammonium salts momentarily prevent the separation of the cadmium hydroxide; but on boiling the tartrates with a slight excess of alkali, ammonia is expelled and precipitation takes place.

J. T.

**Methods of Analysing Columbates containing Earthy Oxides.** By J. L. SMITH (*Chem. News*, **51**, 289—291; 304—307. Compare *Abstr.*, 1884, 111—113).—Up to the present time, samarskite has been found to contain the following earthy oxides:—Yttria, erbia, terbia, phillipia, decipia, thoria, mosandria, and oxides of didymium and cerium. The quantities of such present is not yet known, however; there is about 0.50 per cent. of thoria, whilst of the last two there are merely traces. D. A. L.

**Standardising Solutions of Potassium Permanganate.** By G. KRÜSS (*Ber.*, 18, 1580—1585).—The strength of permanganate solutions can be quickly and accurately determined by Vierordt's method of quantitative spectrum analysis. A. J. G.

**Delicate Test for Antimony.** By O. C. S. CARTER (*Chem. News*, 51, 267—268).—Experiments on the delicacy of the well-known test for antimony, in which the metal is precipitated on platinum in contact with zinc. In this way a light brown stain is obtained from 1 c.c. of a solution containing 0.0001 gram of potassium antimony tartrate = 0.00003614 gram of antimony, whilst 1 c.c. of a solution containing 0.0001807 of antimony gives a black stain covering 1 square centimetre of platinum. The pieces of zinc may conveniently be globular. By winding fine zinc wire round platinum wire, the latter is stained by immersion in extremely dilute antimony solutions.

D. A. L.

**Delicate Tests for Antimony, Arsenic, and Tin.** By S. RIDEAL (*Chem. News*, 51, 292).—By immersing in acid solutions of antimonious chloride a couple consisting of fine platinum wire wound closely round a piece of iron wire, a distinct black stain is obtained on the platinum even with 1 c.c. of a solution = 0.000012 gram antimony. In a similar manner, using fine copper wire instead of the platinum, a grey film of arsenic is obtained with 1 c.c. of arsenious acid solution = 0.0000075 gram arsenic; whilst 1 c.c. of a solution of stannous chloride = 0.00003 gram tin, deposits a film on the gold of a zinc and gold wire couple. Hydrogen sulphide indicates by a precipitate 0.00006 gram antimony and 0.00004 gram arsenic, and by a faint coloration 0.000024 of the former and 0.00002 of the latter metal. By means of decinormal silver nitrate and subsequent addition of ammonia, a perceptible precipitate is obtained with 1 c.c. of a solution containing 0.0000049 of arsenic. The platinum-zinc test (preceding Abstract) detects 0.00003614 gram antimony. D. A. L.

**The Estimation of Ethyl Nitrite in the Spirit of Nitrous Ether and Kindred Preparations.** By A. H. ALLEN (*Pharm. J. Trans.* [3], 15, 673—675).

**Estimation of Spirit of Nitrous Ether.** By D. B. DOTT (*Pharm. J. Trans.* [3], 15, 697—698).

**Detection of Phenol in Creasote.** By P. MCEWAN (*Pharm. J. Trans.* [3], 15, 754—755).—Five drops of spirits of nitrous ether are placed in a test-tube, a drachm of a 0.2 per cent. aqueous solution of the creasote to be examined is added, finally the same volume of strong sulphuric acid is poured in; the formation of a pink ring indicates the presence of phenol, which is confirmed by the production of a pinkish froth on agitating the liquid mixture. D. A. L.

**The Reducing Power of Certain Sugars towards Fehling's Solution, and a Method for the Quantitative Estimation of the same.** By C. KRUIS (*Chem. Centr.*, 1885, 313—315).

**The Time Element in Gluten Determinations.** By W. FREAR (*Amer. Chem. J.*, **6**, 402—403).—The author has made experiments on Beccari's method for determining gluten in grain or flour in order to ascertain the influence which the length of time which elapses between the preparation of the dough and the separation of the starch, exerts upon the quantity of gluten obtained. His results show that the formation of gluten is practically complete in from 45 minutes to an hour after the dough is prepared. The adoption of a longer period is detrimental to the accuracy of the determination, as the dough becomes covered with a hard pellicle, that, on washing, breaks into small pieces, which are very apt to be washed out with the starch carrying a portion of the gluten incorporated with them.

L. T. T.

**Valuation of Acetate of Lime.** By A. A. BLAIR (*Amer. Chem. J.*, **7**, 26—32).—The colour of commercial acetate of lime is often sufficient to seriously affect the volumetric estimation (precipitation of the filtered solution with a known excess of sodium carbonate, filtration and determination of excess of sodium carbonate by standard sulphuric acid). The colour is, however, easily removed by filtration through animal charcoal.

H. B.

**Estimation of the Combined Acids in Plant Sap.** By H. DE VRIES (*Chem. Centr.*, 1885, 394).

**Hübl's Method for the Examination of Oils and Fats.** By R. W. MOORE (*Amer. Chem. J.*, **6**, 416—419).—This method (Abstr., 1884, 1435), whilst valuable for detecting adulteration in many oils, is valueless as a test for the purity of butter, as it would not detect the addition of cocoa-nut oil or a mixture of oleomargarine and cocoa-nut oil. The author considers Reichert's to be the only satisfactory test for butter at present known.

L. T. T.

**Estimation of Fat in Milk.** By E. GEISSLER (*Chem. Centr.*, 1885, 237—238).—In order to obtain accurate results by Wolff's method certain precautions are necessary. If the temperature of the milk and ether is below 18°, the emulsion will not easily separate. 50 c.c. of the milk is measured out at a temperature a little above 18°, mixed with 3 c.c. potash solution (sp. gr. 1.145), and vigorously shaken with 54 c.c. of ether. The shaking must be repeated every five minutes until small bubbles of air appear in the liquid and form a froth on the surface. This will take a longer or shorter time as the milk is poorer or richer in fat. Should the ether not show signs of separation after standing for 15 minutes, the mixture should be warmed in a bath to 20—25°. In extreme cases acidify with hydrochloric acid, and then add a slight excess of caustic potash solution. The results obtained by this method agree very well together.

J. K. C.

**New Reaction of Digitaline.** By P. LAFON (*Compt. rend.*, **100**, 1463—1465).—When a trace of digitaline is treated with a mixture of equal parts of pure sulphuric acid and alcohol, and then mixed with a drop of ferric chloride solution, a greenish-blue coloration is

developed and persists for some hours. Only a very small quantity of digitaline should be used, and this is moistened with a very small quantity of the acid and alcohol, gently heated until it acquires a slight yellow tint, and then mixed with one drop of dilute ferric chloride solution. The coloration becomes more intense on standing and cooling.

This reaction was given by samples of digitaline from five different French makers, but was not obtained with some samples of foreign origin, notably two prepared by Merck. The French samples gave a green coloration with concentrated hydrochloric acid, and a blackish-brown coloration with concentrated sulphuric acid, whilst Merck's crystallised digitaline gave no coloration with the first, and a red coloration with the second reagent. The different samples of digitaline also differed to a marked extent in their solubility in chloroform, and, as Laborde and Duquesnel have recently shown, in their physiological action.

The above reaction is not given by any of the ordinary alkaloids or glucosides.

C. H. B.

**Detection of Magenta in Extract of Archil.** By A. KERTÉSZ (*Dingl. polyt. J.*, **256**, 281).—A small quantity of the extract is boiled with a large amount of water and filtered. The clear filtrate is treated with benzaldehyde, a tin salt, and hydrochloric acid, and the mixture allowed to remain a few minutes after being well shaken. If magenta is present the lower layer assumes a red colour, but remains colourless if magenta is absent. The reaction admits of the detection of 1 part of magenta in 1000 parts of archil extract.

D. B.

**Indigo Testing.** By C. RAWSON (*Chem. News*, **51**, 255—256). Rau's method of indigo testing (this vol., p. 934) does not estimate the indirubin, inasmuch as it is soluble in alcohol and therefore is not found in the crystalline precipitate. The indirubin has great tinctorial power, and plays an important part in indigo dyeing; it should therefore be determined (comp. this vol., p. 697).

D. A. L.

**Detection of Aloes in Mixtures.** By R. A. CRIPPS and T. S. DYMOND (*Pharm. J. Trans.*, [3], **15**, 633—634).—1 grain of substance is dissolved in 16 drops of strong sulphuric acid, 4 drops of nitric acid (sp. gr. 1.42) are added, and the whole diluted with 1 oz. of water; a deep orange or crimson colour changing to a more or less deep claret colour on the addition of ammonia, indicates the presence of aloes. Substances containing chrysophanic acid behave in a similar manner, but, with the exception of senna, may easily be distinguished from aloes, as their aqueous solutions are turned pink by ammonia, whereas the nearly colourless solutions of aloes are not.

D. A. L.

**Separation of Casein from Albumin by Human Milk.** By F. HOPPE-SEYLER (*Zeit. physiol. Chem.*, **9**, 533). Strictures upon recent criticisms of Biedert's (*ibid.*, 354).

C. F. C.

## Technical Chemistry.

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### Relation of Antiseptic Power to Chemical Constitution.

By J. R. DUGGAN (*Amer. Chem. J.*, 7, 62—64).—*Bacillus subtilis* was used for the following determinations; the numbers given are the amounts of material required to prevent fermentation in 10,000 parts of a solution of beef peptones:—Salicylic acid, 4; metahydroxybenzoic acid, 6; parahydroxybenzoic acid, 8; phenol, 20; catechol, 20; resorcinol, 25; quinol, 30; pyrogallol, 15; methyl alcohol, 300; ethyl alcohol, 500; normal propyl alcohol, 200. H. B.

### Orthohydroxybenzenesulphonic Acid.

By E. SERRANT (*Compt. rend.*, 100, 1465—1466).—This acid has about treble the antiseptic power of phenol, and, moreover, is soluble in water in all proportions, has very little corrosive action, and is practically non-poisonous. The author proposes to give it the name *Aseptol*. C. H. B.

### Poisoning by Canned Goods.

By J. G. JOHNSON (*Chem. News*, 51, 268—272).

### Preparation of Chlorine from Magnesium Oxychloride.

By W. WELDON (*J. Soc. Chem. Ind.*, 1885, 171—177, and *Dingl. polyt. J.*, 256, 368).—For the production of chlorine from magnesium oxychloride, obtained by the addition of magnesia to magnesium chloride, a furnace is used which is constructed on the principle of a baker's oven. It consists of a series of vertical chambers, the thickness of the dividing walls of which is considerably greater than the width of the spaces between them. Before charging these chambers with magnesium oxychloride, products of combustion are passed through them until their dividing walls are raised to a certain temperature. The chambers are then charged, and air is introduced, the oxygen of which reacts on the oxychloride, a mixture of chlorine, hydrogen chloride, nitrogen, and excess of air passing off.

Whilst by the old Weldon process, 30 per cent. of the chlorine contained in the hydrochloric acid is yielded as free chlorine, and 70 per cent. converted into calcium chloride, by the magnesium oxychloride process 50 per cent. is obtained as free chlorine and the other 50 per cent. as hydrogen chloride. The operation by which the chlorine is separated from the hydrogen chloride yields the chlorine cool, no operation for the special purpose of cooling the chlorine before its conversion into bleaching powder being thus required.

The manufacture of bleaching powder from dilute chlorine is now conducted at Salindres in mechanical chambers. They are said to prevent all loss of chlorine, and owing to the fact that it is produced at a lower temperature, the bleaching powder is much more uniform in quality and more stable than that manufactured by the ordinary method. D. B.



**Preparation of Chlorine.** By C. TAQUET (*Dingl. polyt. J.*, 256, 274).—The utilisation of the calcium chloride residues obtained in the manufacture of ammonia soda for the production of chlorine is effected by treating the residues with pure silica and manganese dioxide. The following reaction takes place:— $\text{CaCl}_2 + \text{MnO}_2 + 2\text{SiO}_2 = 2\text{Cl} + \text{CaSiO}_3 + \text{MnSiO}_3$ . The concentration of the liquors is performed in cast-iron pans, and the drying operation in a second vessel. If the calcium chloride contains moisture, chlorine and hydrogen chloride are obtained thus:  $2\text{CaCl}_2 + \text{H}_2\text{O} + \text{MnO}_2 + 3\text{SiO}_2 = 2\text{Cl} + 2\text{HCl} + \text{MnSiO}_3 + 2\text{CaSiO}_3$ . By the combined action of these gases on manganese dioxide the hydrogen chloride is decomposed into chlorine, manganous chloride being formed according to the equation  $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + 2\text{Cl}$ . D. B.

**Preparation of Ammonia.** By A. FELDMANN (*Dingl. polyt. J.*, 256, 287).—The author found that the distillation of ammonia is considerably retarded by the presence of the lime sludge, and therefore recommends the treatment of the crude ammonia water or gas liquor with milk of lime, in a vessel provided with an agitator. The mixture is then passed through filter-presses or machined, and the liquid subjected to distillation in the column apparatus. D. B.

**Recovery of Sulphur from Alkali Waste.** (*Dingl. polyt. J.*, 256, 416).—According to Opl, the sulphur of soda waste is said to enter into solution as calcium hydrosulphide on treating the waste with hydrogen sulphide. According to a process patented by v. Miller and Opl this solution is evaporated, the calcium hydrosulphide being decomposed into hydrogen sulphide and free calcium hydroxide. Divers considers both propositions impracticable, as hydrogen sulphide acts only slowly on soda waste, whilst the decomposition of the solution on boiling is very imperfect. Another objection to the process, according to Divers, is the necessity of having to force or pump the gas into the closed vessel holding the waste.

Weldon (*J. Soc. Chem. Ind.*, 1885, 171) is of opinion that the above objections are quite unjustifiable, and are based on erroneous conclusions. The recovery of sulphur from alkali waste by means of hydrogen sulphide has been worked at Hrüschau for about two years on a commercial scale. No pumping is necessary, as the hydrogen sulphide is absorbed as rapidly as it can practically be supplied.

D. B.

**Decomposition of Soda Waste by means of Carbonic Anhydride.** By W. J. KEMP (*J. Soc. Chem. Ind.*, 1885, 144, and *Dingl. polyt. J.*, 256, 321).—The author's experiments were carried out in connection with the process patented by F. B. Rawes. Soda waste was suspended in a dilute solution of sodium hydrogen carbonate, and exposed to a current of carbonic anhydride, the mixture being stirred during the whole of the operation. The sodium hydrogen carbonate is said to act as a carrier of carbonic anhydride, facilitating and expediting the expulsion of the hydrogen sulphide. For the absorption of the gas a series of glass bottles was employed, provided with stirrers, worked by a small electric motor. The bottles were placed in

a water-bath, heated at 45°. The escaping gas was passed through a copper solution for the purpose of absorbing the hydrogen sulphide, whilst the carbonic anhydride was absorbed with aqueous potash. By employing three absorption bottles, and working with a weak current of carbonic anhydride, it was possible to obtain a gas containing 96 per cent. of hydrogen sulphide. When more powerful currents were passed through the bottles, the composition of the gas ranged between 80—90 per cent. hydrogen sulphide, and 20—10 per cent. carbonic anhydride.

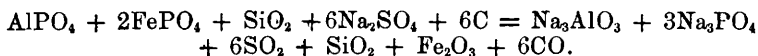
The author is of opinion that this process can be worked with success on a large scale. The weak point, however, appears to be the difficulty of procuring pure carbonic anhydride on a commercial scale.

D. B.

**Preparation of Sulphuric Anhydride.** By A. B. NOBEL and G. FEHRENBACH (*Dingl. polyt. J.*, **256**, 316).—The authors obtain sulphuric anhydride by heating sulphuric acid (monohydrate or English sulphuric acid) with anhydrous or concentrated phosphoric acid. For this purpose a vessel made of platinum, glass, or other suitable substance, is charged with glacial phosphoric acid, and heated on a sand-bath at 320°. Sulphuric acid in the form of vapour is then passed through the vessel, the result being the production of vapours of sulphuric anhydride, which are condensed and collected in the usual manner. The phosphoric acid is concentrated by redistillation and used for a fresh operation.

D. B.

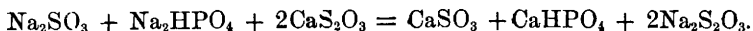
**Treatment of "Redonda" Phosphate.** By W. J. WILLIAMS (*J. Soc. Chem. Ind.*, 1885, 148—151; and *Dingl. polyt. J.*, **256**, 278—279).—Redonda phosphates are generally first calcined or roasted, then intimately mixed with salt cake and coke, and roasted in a reverberatory furnace for two hours. Towards the end of the operation the temperature must be sufficiently high to oxidise the whole of the sulphur, and expel it as sulphurous anhydride. On lixiviating the furnace mass a solution of trisodium phosphate ( $\text{Na}_3\text{PO}_4$ ) and sodium aluminate is produced, leaving an insoluble residue of silica and ferric oxide. The following equation illustrates the reaction which occurs:—



For the purpose of separating the phosphoric acid and alumina, the author originally proposed the treatment of the mixed solution with sulphurous anhydride, but it was found that the precipitated alumina invariably contained phosphoric acid. This difficulty was then overcome by the expedient of crystallising out the trisodium phosphate. By two crystallisations it was possible to obtain a solution of aluminate containing only 1.5—1.2 per cent. of the phosphoric acid originally present in the liquors. This solution was then treated with the sulphurous anhydride from the furnace by means of ordinary condensing towers, and the resulting sludge of alumina was forced through filter-presses, washed and dried. It was found to be practically impos-

sible to wash the alumina completely free from alkali salts. The sodium sulphite was evaporated to dryness, and utilised for fresh furnacings.

As the sale for trisodium phosphate is very limited, it was decided to convert it into calcium phosphate; this could not be effected on the large scale by precipitation with lime, calcium carbonate, or gypsum, as the calcium phosphate invariably contained large quantities of lime, &c. (as much as 26 per cent.). It was then found that by treating the sodium phosphate solution with a thiosulphate solution, obtained by further oxidising "alkali waste," tricalcium phosphate, containing about 95 per cent.  $\text{Ca}_3(\text{PO}_4)_2$ , was formed. For the production of dicalcium phosphate, the trisodium phosphate was first converted into disodium phosphate by treatment with sulphurous anhydride. On subsequently treating the mixed solution of phosphate and sodium sulphite with calcium thiosulphate, pure dicalcium phosphate was not, however, obtained, but a mixture of the latter with calcium sulphite. This reaction takes place according to the following equation:—



To prevent the production of calcium sulphite, the sodium sulphite had to be oxidised into sulphate by injecting air into the mixed solution.

This method being somewhat expensive, the author heated a mixture of phosphates with salt in the presence of hydrogen. For this purpose a mixture of phosphate, coke, and salt was ground together, moistened, laid out in thin cakes, dried, and heated to redness in a cylindrical furnace, a current of steam and air being forced through. Thus 90 per cent. of the phosphoric acid in the "Redonda" phosphate was converted into trisodium phosphate, from which calcium phosphate was produced by the addition of calcium chloride. To produce dicalcium phosphate the requisite quantity of hydrochloric acid is added before precipitation.

D. B.

#### **Cryolite Glass.** By C. WEINREB (*Dingl. polyt. J.*, 256, 361—367).

—The author has made a series of experiments to determine which of the constituents of cryolite occasions the opalescence of cryolite, opal, or bone glass. Analyses of the glass showed that its formation depended on the presence of (1) the aluminium; (2) the fluorine; and (3) the fluorine and aluminium contained in cryolite. It was found that opal glass could not be obtained from either alumina or sodium fluoride, but that for its production the presence of both constituents was necessary.

Probably aluminium fluoride is formed which dissolves in the fused glass, and is deposited on cooling in a finely divided form, producing a milkiess in the glass.

Attempts to convert fluorspar into sodium fluoride by fusion with soda have given satisfactory results, and the author considers the utilisation of fluorspar for the production of opal glass of sufficient importance to receive the attention of glass manufacturers.

D. B.

**Clays.** By KOSMANN (*Dingl. polyt. J.*, **256**, 276—278).—The author has examined refractory plastic clays from Upper and Lower Silesia. He gives the composition of different clays occurring at Schönowitz, the bed having a depth of 10 metres, and extending over an area of 25 hectares. The specimens were dried at 100°, and gave by analysis:—

	I.	II.	III.	IV.	V.
SiO <sub>2</sub> soluble . . . .	33·76	34·95	27·74	37·09	21·19
SiO <sub>2</sub> insoluble . . .	27·91	25·08	41·81	19·19	57·71
Al <sub>2</sub> O <sub>3</sub> . . . . .	25·32	26·21	20·83	32·99	14·74
FeO . . . . .	3·62	3·63	1·55	1·62	—
CaO . . . . .	traces	—	—	—	—
MgO . . . . .	0·46	0·35	0·23	0·32	—
Alkalis . . . . .	2·40	2·10	2·14	1·42	—
H <sub>2</sub> O . . . . .	6·33	7·57	5·57	7·35	6·27

I. Colour, bluish to greenish-white; from the northern part of the bed.

II. Colour, pure white; from the same place.

III. Colour, yellowish-white; from the south-western part of the bed.

IV. Colour, pale blue; adjoining the latter place.

V. Colour, white; a sandy clay from the north-western part of the bed. Clays from Beckern, near Striegau, had the following composition:—

	SiO <sub>2</sub> sol.	SiO <sub>2</sub> insol.	Al <sub>2</sub> O <sub>3</sub>	FeO.	MnO.	CaO.	MgO.	Alkalis.	H <sub>2</sub> O and loss by ignition.
Grey..	43·74	6·97	34·64	2·71	0·34	traces	0·24	1·47	9·88
Blue..	43·31	5·88	36·50	2·00	—	0·63	0·85	1·22	9·60

According to Seger, Meissen kaolins from Lößthain-Kaschka (I), and Kemmlitz (II), gave by analysis—

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO.	K <sub>2</sub> O.	H <sub>2</sub> O and organic matter.
I . . .	51·39	35·44	0·72	0·75	0·80	11·23
II . . .	54·66	31·87	0·50	0·88	0·89	11·58

	Clay substance (Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> + 2H <sub>2</sub> O).	Quartz.	Felspar.
I . . . . .	89·09	9·92	0·99
II . . . . .	80·84	19·64	traces

D. B.

**Silvering of Glass and Mirrors.** By M. HERZOG (*Chem. Centr.*, 1885, 349—351).

**Natural Gas.** (*Pharm. J. Trans.* [3], **15**, 582—584.)

**Composition and Heat of Combustion of Coal from Ruhr.** By SCHEURER-KESTNER (*Compt. rend.*, **100**, 1298—1301).—This coal

contains on an average 10—14 per cent. of ash, but the sample actually used contained a much lower proportion. The combustible portion of the coal had the composition C 89.92; H 4.11; N 1.00; S 1.00; O 3.97 = 100.00, and all the calculations are based on these numbers. The mean of three concordant determinations of the heat of combustion is 9111 cal., whilst the heat of combustion calculated by means of Dulong's formula from the composition of the coal is 8560.6 cal. In other words the actual heat of combustion is 382 cal., or 4.3 per cent. higher than the theoretical value. In this respect the coal from Ruhr agrees with the numerous other samples of coal previously examined by Mennier-Dollfus and the author. Examination of this and previous determinations also shows that the heat of combustion of a coal is higher the greater the proportion of non-volatile carbon (coke) which it contains.

C. H. B.

**Manufacture of Sugar and Purification of Beet-juice by Means of Magnesia and Alumina.** By JÜNEMANN (*Bied. Centr.*, 1885, 358).—The alumina solution is obtained by dialysis of alumina dissolved in aluminium chloride or sulphate; the use of this soluble alumina produces a juice almost absolutely pure. A solution of magnesium hydroxide added to hot syrup, produces a granular crystallisation of insoluble magnesium saccharate.

E. W. P.

**Preparation of Sugar from Sorghum Saccharatum.** By O. KOHLRAUSCH (*Bied. Centr.*, 1885, 349—350).—This is a further report on the manufacture of sugar and cultivation of sorghum (compare this vol., p. 833). The crude juice at 15—18° B., generally contains 2.89 per cent. glucose, 4—5 per cent. of non-saccharine matter, and 9—12 per cent. of saccharose; the coefficient of purity being 48—70. The results obtained in the sugar factory are not satisfactory enough to warrant the cultivation of the plant for profit, but as a source of spirit nearly free from fusel oil it is worthy of attention. Glucose can readily be prepared from sorghum seed, which contains 63 per cent. starch; 5 per cent. of tannin seems to have no prejudicial action.

E. W. P.

**Chemical Composition of the Products of Roller-milling of Wheat.** By C. RICHARDSON (*Amer. Chem. J.*, 6, 388—402).—In continuation of his previous work (this vol., p. 585), the author gives the results of the analyses of 98 samples of roller-milled wheats from Minnesota, Virginia, and Ohio. These include fine flours (*middlings*, *patent flour*, *chop*, &c.), and also the numerous other products and bye-products (such as *germ*, *shorts*, *bran*, *cockle*, *tailings*, &c.) which are produced in roller-milling. This process consists, briefly, in preparing the wheat for the rolls, or breaks, by the removal of foreign seed, dirt, chaff, and certain parts of the outer coatings of the grain; putting the cleaned grain through a series of rolls, after each of which all the reduced portion is removed and collected as *chop*, the coarse material being cleaned from all adherent matter and fed to the following roll until it comes from the last one as mere bran; purifying the various chops by appropriate machinery, which removes *shorts*,

dusty particles, &c., and grades the coarser part—consisting of the interior or floury portions of the grain—into *middlings* of various sizes; purification of these middlings from all foreign matter; reduction of the purified middlings between rolls or with stones (in the first manner flattening the germ so that it can be removed in the bolt); and mixing the graded flours for the market. The *chops* and *middlings* (which really consist principally of endosperm) contain less fibre, ash, oil, and albuminoids than the whole wheat; the *bran* contains much more nitrogen, ash, oil, and fibre than the chops, but not necessarily more gluten: the *shorts* are poorer in oil, fibre, and ash than the bran: the *germ* is poor in carbohydrates, but very rich in oil and albuminoids (sometimes giving as much as 15 per cent. and 32 per cent. of the two latter respectively), and contains no gluten. The five classes of *middlings*, graded by sizes, present a regular decrease in ash, oil, and fibre, from the largest to the lowest, but the albuminoids do not vary much. The *patent flour* has the greatest number of desirable qualities.

“The results, as a whole, warrant the conclusion that less gluten is wasted in the bye-products than would be imagined,” and appear to show that the hard spring wheats are more suited to the process than the softer winter varieties. The chief fault of the high grade flours obtained by this process is their deficiency in phosphates, a great portion being lost in the bye-products.

The full analytical results are carefully tabulated, and the author also refers, for further details, to Bulletin No. 4 of the Bureau of Chemistry, United States Department of Agriculture. L. T. T.

**Creaming by Centrifugals on Various Systems.** By M. SIEWART (*Bied. Centr.*, 1885, 344—346).

**Oberbockstruck's Milk Refrigerator.** By WÜST and KIRCHNER (*Bied. Centr.*, 1885, 343—344).

**Three Chinese Fixed Oils.** By R. H. DAVIES (*Pharm. J. Trans.*, [3], 15, 634—636).—The following new oils from China have been examined. Tea oil from *Camellia oleifera* resembles olive oil, but has a characteristic odour and taste. Its sp. gr. is 0·9175 at 15·5°. Solid matter separates, but it does not solidify at —13·3°. 100 parts of oil require 0·34 part of potash to neutralise the free acidity, and 19·55 parts of potash for saponification; it contains 93·92 per cent. of insoluble fatty acids, of which 83·15 per cent. is oleic, the remainder being probably a stearic acid. *Cabbage oil* from *Brassica*, *sp.*, resembles rape oil, has a strong disagreeable odour, sp. gr. 0·914 at 15·5°, and forms a bright orange-yellow mass at —12°. 100 parts of oil require 0·125 part of potash for neutralisation, and 17·52 parts of potash for saponification. The oil yields 95·32 per cent. of insoluble fatty acids, consisting mainly of an acid resembling brassic acid. *Wood oil* from *Elæococcus cordata* is brown in colour, has a persistent and disagreeable odour, and is remarkable for its great drying properties. Its sp. gr. is 0·94015 at 15·5°; it does not solidify at —13·3°. Sulphuric acid carbonises it, whilst nitric acid forms a solid orange-yellow nitro-

derivative. The free acidity of 100 parts of this oil neutralises 0.39 part potash; the oil requires 21.1 parts of potash for saponification, and yields 94.10 parts of insoluble fatty acids; by crystallising this latter from alcohol, crystalline plates melting at  $67^{\circ}$  are obtained. This oil is distinct from Gurgun balsam, also known as wood oil.

D. A. L.

**Japanese Oils.** By E. M. HOLMES (*Pharm. J. Trans.* [3], 15, 636—638). The author remarks on three Japanese oils, namely, brassica, camellia, and wood oil, which are similar to the Chinese oils described in the preceding Abstract.

D. A. L.

**Preparation of Soaps from Oil Seeds.** By B. SEEMAN (*Dingl. polyt. J.*, 256, 287).—The kernels of cocoa-nuts, palm-nuts, and the seeds of the cotton plant, &c., are crushed and boiled with soda-ley of  $20^{\circ}$  B. until the combination of the oil in the seeds with the soda is completed. The husks and shells of the seeds and kernels are deposited by salting out or adding a strong solution of soda. The soap is then separated from the leys by a further process of salting out.

D. B.

**Preparation of Thallin.** (*Dingl. polyt. J.*, 256, 192).—In order to obtain tetrahydroparaquinanisoil,  $C_{10}H_{13}NO$ , called "thallin," the Baden Aniline and Soda Works propose heating 4 kilos. granulated tin, 15 kilos. hydrochloric acid of 1.14 sp. gr., and 1 kilo. paraquinanisoil hydrochloride, on a water-bath for 8 to 10 hours. The stannochloride is converted into the zinc salt, from which the base is isolated by the addition of potash, an oil being obtained which solidifies on cooling in the form of pale yellow crystals. The product is sparingly soluble in cold, more readily in hot water, readily soluble in alcohol, ether, and light petroleum. It melts at  $42\text{--}43^{\circ}$ , and boils at  $282\text{--}283^{\circ}$  without decomposition. Its solution assumes a deep green coloration when treated with ferric chloride, potassium dichromate, or chlorine-water; this reaction is very sensitive, and is a type of the base and its salts; hence the name "thallin."

D. B.

**Goods Printed with Artificial Indigo.** By H. A. COSTOBADIE (*Dingl. polyt. J.*, 256, 90).—The author states that propiolic acid paste ( $C_9H_5NO_4$ ) is still used by several printers for the production of special shades. It is said to possess many advantages over the natural dye, being fixed to the cloth with greater ease, and producing more brilliant and durable effects. The author employs the propiolic acid for light shades, in which case the printing colour costs only about 80 pfennigs per kilo. The treatment of the printed goods is very simple. After hanging for 12 hours or more at  $25^{\circ}$  so as to develop the blue completely, the goods are washed, soaped at  $75^{\circ}$ , dried, and passed through Mather and Platt's steaming apparatus. This short passage suffices to remove the unpleasant odour which clings to the cloth (originating from a volatile mercaptan ether). Several receipts for printing with artificial indigo are given in the original paper.

D. B.

**Tannin Method of Fixing Colouring Matters on Cotton.** By O. N. WITT (*Chem. News*, 51, 217—218).—Basic aniline dyes are generally fixed on cotton by the formation upon the fibre of insoluble tannin compounds—tannin lakes. To precipitate the dyes completely it is necessary to use, in addition to the tannin, sodium carbonate, or other base, to combine with the acid set free from the colouring matter. Most basic colours are polybasic, forming several tannates, and insoluble tannates when treated with tannin solutions unite with more tannin and become soluble. Therefore, the fabric must be first saturated with the required quantity of tannin solution, and then dyed in the colour. As tannin-lakes are soluble in acetic acid, cloth is printed with a mixture of tannin and colour in the proper proportions, with acetic acid, gum or starch to thicken, and sodium acetate to take up any liberated acid. On steaming the acetic acid dissolves the lake, enabling it to penetrate the material, volatilises, and leaves the coloured lake insoluble upon the fibres. There may, however, readily be excess of tannin on the fibre, consequently during washing a portion of the lake is dissolved by this excess, and the colour is reprecipitated by the lime of the water on the whites and other colours. Many substances have been suggested to render the excess of tannin harmless, but none have succeeded so well as antimony. In dyeing, a bath of potassium antimony tartrate, or better still oxalate, is introduced between the tannin and colour-bath; in printing, the printed and steamed pieces are passed into the hot antimony bath. After the antimony treatment, thorough washing is necessary. The antimony first forms an insoluble tannate, hence renders the tannin harmless; it subsequently enters into the fixed colours, forming antimony-tannin-lakes, which are not readily soluble. From the removal of antimony in the colour on the fabric, the antimony bath gradually becomes more and more charged with hydrogen potassium tartrate or oxalate, and ultimately the tartrate, owing to its solvent action, becomes more injurious to the dyed fabric than the excess of tannin itself; the hydrogen potassium oxalate, on the other hand, is not such a good solvent for the antimony-tannin-lakes, and therefore potassium antimony oxalate is recommended to supersede the corresponding tartrate in antimony-lakes. D. A. L.

**Casein-glue, a Substitute for Gum Arabic.** By R. KAYSER (*Dingl. polyt. J.*, 256, 96).—On account of the present high price of gum arabic the author tried the following preparation:—Casein was prepared by heating milk with a small quantity of tartaric acid. The mass was then treated with a solution containing 6 parts of borax in 100 of water, and warmed gently until the whole of the casein had been dissolved. The resulting solution possesses considerable tenacity, is inexpensive and durable, and may be used as a substitute for gum arabic in cases where the latter cannot be replaced by dextrose. D. B.

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## General and Physical Chemistry.

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**Spectrum Lines of Hydrogen.** By J. J. BALMER (*Ann. Phys. Chem.* [2], **25**, 80—87).—In this paper an attempt is made to trace out a mathematical ratio between the wave-lengths of the hydrogen lines. The general formula deduced is  $\lambda = \frac{m^2}{m^2 - n^2} \cdot h \frac{mm}{10^7}$ . The value for  $h$ , which may be called the basic number for hydrogen, is 3645·6; the values for  $m$  and  $n$  in the fraction are always integers. Thus, on comparing the wave-lengths of the three more common lines calculated according to the above equation with the wave-lengths observed by Ångström, the difference is found to be less than  $\frac{1}{40000}$  of a wave-length:—

	Observed.		
H <sub>α</sub> (E line) = $\frac{9}{5}h = 6562\cdot08$	6562·1	$m = 3$	$n = 2$
H <sub>β</sub> (F line) = $\frac{4}{3}h = 4860\cdot8$	4860·74	$m = 4$	$n = 2$
H <sub>γ</sub> (A line) = $\frac{9}{8}h = 4101\cdot3$	4101·2	$m = 6$	$n = 2$

The wave-lengths for the violet lines and ultra-violet lines of the fixed stars observed by Huggins are compared with those calculated in accordance with the above formula, and the difference is within the limits of experimental error. V. H. V.

**Spectrum of Ammonia with a Reversed Induced Current.** By L. DE BOISBAUDRAN (*Compt. rend.*, **101**, 42—45).—When an induction spark falls upon an aqueous solution of ammonia, the liquid itself being the positive pole, a yellow globular or cup-shaped arc is formed between the two poles, and at the upper surface of the liquid pole there is a thin but very distinct greenish disc. This disc is not a true phosphorescence, but is due to the illumination of ammonia-vapour by the positive portion of the discharge; it gives a spectrum of one band in the green at 107·3, corresponding with wave-lengths 5681—5643 in the brightest portion. The interpolar yellow arc gives a spectrum consisting of several nebulous bands of various widths situated between wave-lengths 6325 and 5252. This spectrum, with the exception of the band in the green and a band at 6045—6008, is not given by pure and dry ammonia gas, but is only obtained in presence of water or oxygen; it appears to be identical with one of those observed by Mitscherlich (*Phil. Mag.*, **27**, 169), with a flame charged with ammonia. The green band at 5681—5643 is obtained with ammonia gas, and is more intense when the gas is moist.

C. H. B.

**Mutual Extinction of the Spectra of Yttrium and Samarium.** By W. CROOKES (*Compt. rend.*, **100**, 1495—1497).—The spectrum of a phosphorescent mixture of samaria 90 parts, and yttria 10 parts, in high vacua, shows none of the lines of yttrium, but is almost a

facsimile of the spectrum of pure samarium, except that the orange line at 2693 on the  $\frac{1}{\lambda^2}$  scale, which is scarcely visible in the spectrum of the pure substance, becomes sufficiently distinct to be measured. A complete change in the spectrum takes place between very narrow limits when the proportions of the two substances are varied. A mixture of samaria 44 parts, and yttria 56 parts, gives the spectrum of pure samarium (with the exception of the orange line already mentioned); a mixture of samaria 42 parts, and yttria 58 parts, gives bands peculiar to each of the constituents; whilst the spectrum of samaria 39 parts, and yttria 61 parts, is almost the spectrum of pure yttrium.

The orange line at 2693, which is so feeble in the spectrum of pure samarium, is the characteristic line in the spectra of samarium-yttrium mixtures. It attains its maximum intensity with a mixture of samaria 80 parts, yttria 20 parts. When the proportion of samaria is as low as 3 per cent., this line diminishes in intensity, and with pure yttrium it is no longer visible. So long as this line is visible the other lines in the spectra have less than their normal intensity, and several of the bands normally present in the spectra of yttrium and samarium respectively are entirely wanting. It is evident that since the presence of one body may so materially alter the spectrum of another, the indications of the spectroscope ought always to be controlled by chemical analysis.

With a mixture of samarium 1 part, and calcium 100 parts, the spectrum of samarium is very brilliant; with 1 part in 10,000 the bands become less brilliant; with 1 part in 100,000 the green and red bands are almost completely masked by the continuous spectrum of the calcium, but the double orange band and the black space in the yellowish-green are still very distinct. With 1 part in 1,000,000 the orange bands have almost disappeared, but the dark band is still apparent; whilst with 1 part in 2,500,000 the dark band is the only remaining trace of the samarium spectrum.

C. H. B.

**Spectrographic Investigations of Different Standards of Light: their Use in Measuring Photographic Sensitiveness.** By J. M. EDER (*Monatsh. Chem.*, 6, 363—368).—This paper contains an account of the investigations of the light produced by burning amyl acetate, which has been proposed by Abney (*Photographic News*, 1884, 787) as a standard in measuring the photographic sensitiveness of different substances, also of the light given out by Balmain's paint, which is used as source of light in Warnerke's "sensitometer." The first of these lights is less rich in chemically active rays than sunlight, and the second is still less active. Further, the sensitiveness of a substance varies with the quality of the light, and for the same substance the results obtained with either of the above lights is different from that obtained with sunlight.

P. P. B.

**Optical Properties of Thin Metallic Layers.** By W. VOIGT (*Ann. Phys. Chem.* [2], 25, 95—114).

**Reproduction of Siemens' Mercury Unit.** By K. STRECKER (*Ann. Phys. Chem.* [2], 25, 252—273 and 456—487).

**The Seat of the Electromotive Force in the Voltaic Cell.** By O. LODGE (*Phil. Mag.* [5], 19, 153—190; 254—280; 340—365).

—The first paper gives an historical account of the chief experimental researches into the seat of the electromotive force in Volta's effect, and in the voltaic cell; the second discusses the various theoretical views already advanced, and explains those of the author; the third is occupied by the application of these last to certain cognate phenomena. The author maintains that there really is a contact force at every junction of dissimilar substances, whether solid, liquid, or gaseous, and that the electromotive force of a circuit is the sum of such contact forces. But the values ordinarily assigned to given contacts need not be admitted. It is certain, however, that the energy of the voltaic current of a cell is the equivalent of the chemical actions going on within it.

According to the author's views, a piece of clean zinc and one of clean copper, surrounded by air, are each at a lower potential than the air, because the electro-negative oxygen molecules are straining towards the metal, which thus rises in negative potential, not on account of any actual oxidation, but by the approximation of the oxygen molecules. This approximation being due to the chemical affinity between the elements, may be measured by their heat of combination. Calculated on this hypothesis, the potential of bright zinc is 1·8 volt below that of the surrounding air; clean copper 0·8 volt below the air. If the zinc and copper are put into contact, a rush of electricity takes place from the copper to the zinc, so that their potential is equalised (neglecting for the present an electromotive force of one-third of a millivolt developed at the junction, and driving positive electricity from copper to zinc). When the metals are separate, the oxygen-atoms, being all charged with negative electricity, are strained equally on all sides, and could not move in without giving the body an absolute charge. But when the metals are in contact, the oxygen-atoms are cleared away at the place, and the stress being no longer counterbalanced, they can move nearer to the zinc, their electricity finding a passage into the copper, whose surface will thereupon repel the oxygen-atoms to a greater than the normal distance. On comparing the figures to which this theory leads with those obtained by experiment, the author finds that whilst the agreement is not exact, it is, nevertheless, too close to be merely accidental. The effect of the contact is to throw the surrounding medium, if it be a dielectric such as air, into a state of strain; whilst if it be an electrolyte (for instance, dilute acid, in which the oxygen-atoms are subject to precisely the like attractions), a current is conveyed.

Besides this readjustment of the chemical forces, a physical action is brought into play by the contact of dissimilar bodies—an action arising, as the author conceives, from the dissymmetry to which the motions of the molecules are then subjected. This prevents the reduction of two pieces of metal in contact to *exactly* the same potential. Its intensity, which varies with the temperature, can be

measured by the Peltier effect only, and is probably independent of the surrounding media. This force is also related to the Seebeck effect, and in the contact of ordinary metals is very small, because it depends upon the specific resistance. With badly conducting metals, such as antimony and bismuth, and still more with selenium and tellurium, it is much greater. With non-conductors it becomes enormous, but necessarily it can then exhibit electrostatic phenomena only, not currents. Even in these cases mechanical actions, such as friction, may help the movement of the electricity.

The size of atoms, as deduced from electrical data by Sir W. Thomson, is discussed in connection with the author's views, chiefly in relation to the metallic union of mercury and tin, the result being an estimate of the linear molecular dimensions expressed by  $4 \times 10^{-9}$ , which is believed to be correct within narrower limits than those admitted by Thomson.

R. R.

**Electric Conductivity of Gases.** By F. STENGER (*Ann. Phys. Chem.* [2], **25**, 31—48).—In this paper it is shown that the difference between the phenomena of the spark and glow discharge is one of degree, not of kind. The various supposed characteristic differences alluded to by previous writers are discussed, and shown to have no real validity; these are—1st, the intermediate gas-layer possesses a lower resistance in the spark than in the glow discharge; 2nd, in the spark the anode is more strongly heated than the cathode, but conversely with the glow discharge; 3rd, the spectrum of the spark is that of the substance of the electrode, but in the glow discharge is seen only the spectrum of the intermediate gas-layer; 4th, in the spark both the electrodes are equally dissipated, but in the glow only the cathode. These conclusions, partly deduced from original and partly from previous experiments, are in accordance with the observations of Warren de la Rue and H. Müller that a change of pressure of the gas induces the conversion of the spark into the glow discharge. (*Phil. Trans.*, **171**, 65.)

V. H. V.

**Electric Conductivity and Temperature Coefficient of Solid Mercury.** By C. L. WEBER (*Ann. Phys. Chem.* [2], **25**, 245—252).—According to the researches of Matthiessen, the alloys of mercury seem to form a distinct class by themselves as regards their electric conductivity. Siemens explained their peculiar function on the hypothesis that their conductivity was equal to the mean conductivity of their constituents, assuming them to be in the liquid state. Experiments, however, did not confirm this hypothesis. In this paper, an account is given of experiments on the electric conductivity of mercury solidified by solid carbonic anhydride dissolved in ether. The principal results obtained were (i) the conductivity is increased four-fold on solidification; the value referred to,  $0^{\circ}$ , of the solid metal is  $3.5^{\circ}$ ; (ii) the temperature coefficient of the solid mercury, at points sufficiently removed from the point of fusion, is approximately equal to those of other solid metals.

This great difference of the solid and liquid metal probably influences the conductivity of amalgams, solid at ordinary temperatures.

V. H. V.

**Electric Conductivity of Aqueous Alcohol.** By E. PFEIFFER (*Ann. Phys. Chem.* [2], **25**, 232—245).—The curve of the electric conductivity of mixtures of alcohol and water as a function of the percentage proportion of the two constituents shows an alternate rise and fall. Thus it rises with mixtures containing 0—5·24 per cent. alcohol, falls at 5·24 until it reaches a minimum at about 30 per cent., rises from this point until a maximum is attained at 83·4, and falls again. The minimum point corresponds with a mixture of 1 mol. of alcohol with 6 mols. of water, the maximum point, with a mixture of 1 mol. of water and 2 mols. alcohol. These mixtures correspond probably with the formation of definite chemical combinations, of which one possesses a higher, the other a lower, coefficient of conductivity than either of the constituents. V. H. V.

**Validity of Joule's Law for Electrolytes.** By H. JAHN (*Ann. Phys. Chem.* [2], **25**, 49—71).

**Electro-pseudolysis.** By D. TOMASSI (*Bull. Soc. Chim.*, **43**, 418—420).—Although it requires 69 cal. to decompose a molecule of water, yet electric currents of the feeblest strength are capable of separating oxygen and hydrogen from acidulated water; the author considers this result to be due not to electrolysis, but to the simple polarisation and collection of the atoms of oxygen and hydrogen in the free state in the water; their presence being due to slight dissociation taking place at low temperatures. This action is observable in many other cases, as in the action of a feeble electric current on a dilute solution of ammonium chloride, ammonia and hydrochloric acid being formed. This collection, by means of feeble electric currents of the free atoms formed in a solution by dissociation at low temperatures, the author proposes to call electro-pseudolysis. A. P.

**Electro-chemical Studies.** By W. OSTWALD (*J. pr. Chem.* [2], **31**, 433—462).—The enormous increase which the electrical conductivity of weak acids appears to undergo in proportion to their state of dilution has led the author to somewhat modify the opinions expressed in a former paper (this vol., p. 323). The influence exerted by the condition of dilution of any acid is the same in all cases, and may be defined as a function of a certain constant which is peculiar to each acid. The author compares in every case the molecular conductivity of the acid under investigation, the expression being obtained by multiplying the specific conductivity by the volume of the solution containing the molecular weight of the electrolyte in grams. The method recommended by Kohlrausch was employed in taking the measurements, and the different degrees of dilution varied as the whole powers of 2, and were obtained in every case by successive removal of half the volume of solution and its replacement by pure water. The conductivity of strong monobasic acids such as hydrochloric, hydrobromic, hydriodic, nitric, chloric, and perchloric acids varied from about 78 to 89·5 as the dilution increased from 2 to 1024 times that of the normal solution, and appeared to approach a

maximum of about 90; beyond this dilution, the numbers diminished, owing probably to the presence of minute quantities of impurity in the water, which of course made themselves felt in a more marked degree as the dilution increased. As a diminution is observed both in alkaline and acid liquids, the author infers the presence of traces of ammonium carbonate, which he shows has a disturbing influence on both. For the above acids, however, the law holds good that with increased dilution their molecular electric conductivity tends to a maximum which is independent of the nature of the acid.

The weaker acids such as butyric, acetic, formic, &c., begin at the same state of dilution with a much smaller conductivity, which increases, however, with the dilution, but does not arrive near the same maximum before the disturbing influences of the impurities come into play, hence it is impossible to say that they all tend to the same maximum, but they advance in strictly parallel lines, their conductivity at any given stage being the result of the dilution operating on a given constant peculiar to each acid; in other words, the increase of conductivity for each monobasic acid forms part of the same curve.

Polybasic acids appear to follow a different law, according as the different replaceable hydrogen-atoms have stronger or weaker acid qualities. Selenic acid, for instance, behaves like a monobasic acid, and especially like chloracetic; both this and phosphorous acid do not reach a conductivity of 80 at a dilution of 4096 litres. Strong dibasic acids, however, act quite differently; after reaching 90, the second hydrogen-atom comes into play, and the increase begins again to be rapid, reaching in the cases of sulphuric and methylenedisulphonic acids to nearly 180 at a dilution of 4096 litres, thus pointing to a limit which is double that attained by the strong monobasic acids.

Phosphoric acid, being a comparatively weak acid as regards its third replaceable hydrogen-atom, does not increase more rapidly than a monobasic acid. Other tribasic acids have not been brought within the scope of this investigation. In conclusion, the author draws attention to the great change in the electrical conductivity of any acid caused by the admixture of small quantities of other acids; and in opposition to Bouty's theory, is of opinion that the alterations of the general electric conductivity by dilution are not due to the successive formation of different hydrates.

J. K. C.

**Dielectric Constant of certain Gases and Vapours.** By I. KLEMENČIČ (*Phil. Mag.* [5], 19, 393—395).—The paper describes the author's mode of experiment in the determination of dielectric constants. The results in the case of seven gases and of carbon bisulphide agree well with Boltzmann's determinations, and with the electromagnetic theory of light. But the figures obtained for sulphurous acid, ether, ethyl chloride, and ethyl bromide, do not satisfy the conditions of that theory.

R. R.

**Electromagnetic Action of Dielectric Polarisation.** By W. C. RÖNTGEN (*Phil. Mag.* [5], 19, 385—388).—The paper describes an experiment with a rotating ebonite disc, confirming Faraday's theory as to a change of dielectric polarisation exerting

an electromagnetic force exactly like a current in the direction of the displacement of the positive electricity in the insulator.

R. R.

**Specific Heat of Aqueous Alcohol.** By A. BLÜMCKE (*Ann. Phys. Chem.* [2], **25**, 154—165).—In this paper, an account is given of determinations of the specific heat of various mixtures of alcohol and water as a function of the temperature. The results show that there is apparently no direct relation between the specific heat, concentration, and temperature. With mixtures containing 0 to 15·20 per cent. alcohol, the specific heat gradually increases, and from 20—99 per cent. gradually decreases. These results are in accordance with the observations of Dupré and Page (*Phil. Mag.* [4], **38**, 158), and of Schüllen.

V. H. V.

**Thermal Phenomena of Colloids.** By E. WIEDEMANN and C. LÜDEKING (*Ann. Phys. Chem.* [2], **25**, 145—153).—The dissolution of dry colloids, like that of salts rendered anhydrous, is separable into two distinct phenomena, the one, hydration, an exothermic change, the other, solution, an endothermic change. These successive phenomena can be illustrated in the case of anhydrous and hydrated gelatin.

Composition of sample.	Water added.	Heat-change in gram-calories.
2 grams gelatin .....	10 grams.	+ 3·1
„ „ + 100 p. c. H <sub>2</sub> O	8 „	— 1·0

Similar results were obtained with gum arabic, tragacanth gum, dextrin, starch, and tannin. The difference between the thermic phenomena of the solution of a crystalline and amorphous form of the same substance is well illustrated in the case of tartaric acid; thus the solution of crystalline dextrotartaric acid is an endothermic change (— 23·37 cal.), of amorphous inactive tartaric acid an endothermic change (+ 5·92 cal.). A similar relationship exists between crystalline and barley sugar. The coagulation of colloïd silicic acid is accompanied by an evolution of heat (11·8 cal.); this result is in opposition to Thomsen's observations, that there is no heat-change; but the discrepancy is to be explained by the length of time taken by Thomsen in his experiments.

The statement of Guthrie that the tension of aqueous vapour of solutions of colloïds is equal to that of water is incorrect, inasmuch as the boiling point of a solution of gelatin is higher than that of water, and secondly, at low temperatures the admixture of gelatin and water is accompanied by development of heat; and direct experiments with solutions of gum arabic showed that the tension of its solution is less than that of water.

V. H. V.

**Sodium Methoxide.** By DE FORCRAND (*Compt. rend.*, **100**, 1500—1502).—When metallic sodium is added to anhydrous methyl alcohol, the action is more energetic than with ethyl alcohol, and in presence of a large excess of alcohol solution is very rapid. The heat developed at 16° is + 48·2 cal. for Na = 23 grams. Anhydrous sodium meth-

oxide, NaOMe, was prepared by heating the solution at 180—200° in a current of dry hydrogen for several hours. It is a white nacreous highly deliquescent solid; heat of dissolution at 16° = + 11·89 cal. The compound NaOMe.HOMe, is obtained in colourless nacreous deliquescent crystals by drying, on biscuit-porcelain, the crystalline mass resulting from the dissolution of sodium in 5—6 equivalents of methyl alcohol; heat of dissolution at 17° = - 5·05 cal. From these results, it follows that—

CH <sub>4</sub> O liquid + Na solid = CH <sub>3</sub> NaO solid + H gas .....	develops + 33·19 cal.
NaOMe solid + <i>n</i> CH <sub>4</sub> O liquid = NaOMe, diss. in <i>n</i> CH <sub>4</sub> O.....	„ + 15·01 „
NaOMe solid + CH <sub>4</sub> O liquid = NaOMe, CH <sub>4</sub> O solid.....	„ + 8·84 „
2CH <sub>4</sub> O liquid + Na solid = NaOMe, CH <sub>4</sub> O solid + H gas.....	„ + 42·03 „
2CH <sub>4</sub> O liquid + Na <sub>2</sub> O solid = 2NaOMe solid + H <sub>2</sub> O solid.....	dev. + 2 × 18·32 „
CH <sub>4</sub> O liquid + NaHO solid = NaOMe solid + H <sub>2</sub> O solid.....	develops + 1·32 „

These numbers are very similar to those obtained with ethyl alcohol, and almost identical with those obtained by the action of sodium on water. It would seem, therefore, that the molecule of water contained in these alcohols acts on sodium as if it were in the free state. In presence of a large excess of the solvent the numbers obtained are higher with alcohol than with water, a fact which indicates that the dissociation of the alcoholates in presence of alcohol is less than the dissociation of the hydroxide in presence of water. C. H. B.

**Heat of Neutralisation of Hydroxybenzoic Acids.**—By BERTHELOT and WERNER (*Compt. rend.*, **100**, 1568—1570).—*Hydroxybenzoic Acid* (1 : 2).—Heat of dissolution - 6·35 cal.

HO·C <sub>6</sub> H <sub>4</sub> ·COOH diss. + $\frac{1}{2}$ Na <sub>2</sub> O	develops + 12·91 cal.
„ + Na <sub>2</sub> O	„ + 0·81 „
	<hr/> + 13·72 „

*Hydroxybenzoic Acid* (1 : 3).—Heat of dissolution - 6·18 cal.

HO·C <sub>6</sub> H <sub>4</sub> ·COOH diss. + $\frac{1}{2}$ Na <sub>2</sub> O	develops + 13·18 cal.
„ + Na <sub>2</sub> O	„ + 8·52 „
	<hr/> 21·70 „

*Hydroxybenzoic Acid* (1 : 4).—Heat of dissolution - 5·58 cal.; heat of hydration, C<sub>7</sub>H<sub>5</sub>O<sub>3</sub> + H<sub>2</sub>O liquid develops + 2·14 cal.; H<sub>2</sub>O solid + 0·71 cal.

HO·C <sub>6</sub> H <sub>4</sub> ·COOH diss. + $\frac{1}{2}$ Na <sub>2</sub> O	develops + 12·97 cal.
„ + Na <sub>2</sub> O	„ + 9·33 „
	<hr/> 22·30 „



The heat of dissolution, and the heat of neutralisation by the first equivalent of alkali, are practically the same for all three acids, but the meta- and para- differ from the ortho-derivative in that with a second equivalent of alkali they develop an amount of heat practically equal to the heat of neutralisation of phenol, and hence show a marked phenolic as well as acid character. This difference in the behaviour of the three compounds, depending on the different orientation of the substituted radicles, is strictly analogous to that already observed in the case of the ortho-, meta-, and para-di- and tri-hydroxybenzenes (this vol., p. 628). C. H. B.

**Spontaneous Change of Form of Homogeneous Solid Substances, induced by Internal Energy.** By O. LEHMANN (*Ann. Phys. Chem.* [2], 25, 173—189).

**Physico-chemical Experiments.** By V. MEYER and G. G. POND (*Ber.*, 18, 1623—1628).—According to the experiments of Menschutkin and Konowaloff (*Abstr.*, 1884, 1119), tertiary amyl acetate and chloride, when heated to a temperature at which, under ordinary conditions, decomposition does not occur, are to a large extent dissociated in the presence of rough substances, such as sand, asbestos, or particles of glass. In order to test the accuracy of this result, the authors have repeated the experiments with a slight modification. The apparatus is so arranged that as soon as the substance has been volatilised and a constant volume obtained, sand may be dropped in without opening the apparatus. The experiments described do not confirm Menschutkin and Konowaloff's results, as the introduction of the sand did not produce the smallest effect. A. K. M.

**Influence of Temperature on the Capillary Meniscus Angle.** By J. TRAUBE (*J. pr. Chem.* [2], 31, 514—527).—This paper consists of some observations relating to Volkmann's remarks on Schiff's work on the constants of capillarity of liquids at their boiling points (*Abstr.*, 1884, 808). Schiff shows that the meniscus becomes flatter with rise of temperature, and at the critical point becomes convex; the angle of the meniscus with the walls of the tube increases therefore at the same time; the same results were obtained by him with different preparations of the same substance, and at various times. Volkmann assumes that owing to the extreme difficulty of making accurate observations, the values obtained by Schiff are merely accidental. This statement the author opposes, on the ground that he has repeated Schiff's experiments, and obtained in every case confirmatory results, showing that the form of the meniscus undergoes invariably a gradual change with rise of temperature, and that in no case did it present the form of a hemisphere. From his own experiments, he concludes that there exists a certain temperature for every substance at which the meniscus assumes a hemispherical form, but above which it flattens, and its edge-angle increases.

On repeating Link's experiments, the author found that the capillary elevation of a liquid was independent of the substance of the tube, thus obtaining an opposite result to that of Link. J. K. C.

**Application of Various Substances as Halogen Carriers.**

By C. WILLGERODT (*J. pr. Chem* [2], **31**, 539—540).—The author has found that the presence of those elements whose chlorides easily give up their chlorine assists greatly in the chlorination of organic substances. Metallic iron or any of its oxides behave as excellent carriers in this respect; also antimony and tin, their oxides, and to a much less degree bismuth, arsenic, amorphous phosphorus, and sulphur. Sodium, magnesium, zinc, copper, mercury, nickel, and lead, have, however, the opposite effect.

J. K. C.

**Velocity of Saponification.** By L. REICHER (*Annalen*, **228**, 257—287).—Schwab has recently pointed out (*Bydrage tot de kennis der estervorming*, Inaug. Dissert., Amsterdam, 1883) the objections to Menschutkin's mode of determining the initial rate of etherification of alcohols and acids, namely, the influence which the products of the reaction, ether and water, exert on the velocity. He attempted to minimise this influence by using a large excess of alcohol instead of working with a mixture of acid and alcohol in their molecular proportions. He also proposed to substitute the constant of the velocity of saponification for the initial rate of etherification. He endeavoured to determine the value of this constant by decomposing ethereal salts with water. Better results were obtained by the author and also by Warder (*Ber.*, **14**, 1361), who substituted alkalis for water in the reaction.

The author decomposes the ethereal salts with alkaline solutions of known strength in a specially constructed apparatus, in which the temperature is accurately controlled and measured. After a given time, a portion of the mixture is poured into excess of standard sulphuric acid, and the excess of acid determined by titration with baryta-water. In this way, the amount of alkali used and of ether saponified is ascertained. One advantage of the process is that the ethereal salts need not be in a state of absolute purity; they must be free from acids or other impurities which would interfere with the titration, but the presence of alcohol would not interfere with the results.

The constant of the velocity of saponification has been determined for the following ethers and bases:—

With ethyl acetate at 9.4.°		With soda at 9.4.°	With soda at 14.4.°
Soda .....	2.307	Methyl acetate ..	3.493
Potash.....	2.298	Ethyl „ ..	2.307
Lime .....	2.285	Propyl „ ..	1.920
Strontia .....	2.204	Isobutyl „ ..	1.618
Baryta.....	2.144	Isoamyl „ ..	1.645
Ammonia .....	0.011		
		Ethyl acetate....	3.204
		„ propionate ..	2.816
		„ butyrate ..	1.702
		„ isobutyrate ..	1.731
		„ isovalerate. ..	0.614
		„ benzoate ..	0.830

W. C. W.

**Formation of a Stalactite by Vapour.** By J. BROWN (*Phil. Mag.* [5], **19**, 395).—The vapour of anhydrous aluminium chloride

issuing from a crucible, formed by contact with the moisture of the air, a white stalactitic tube of hydrated chloride, about  $1\frac{1}{2}$  inch long and one-tenth inch diameter. The formation seemed quite analogous to that of the ordinary calcium carbonate stalactite. R. R.

**Lecture Experiments on the Occlusion of Hydrogen by Palladium.** By H. SCHIFF (*Ber.*, 18, 1727—1729).—This is a description of experiments for demonstrating the occlusion of hydrogen by palladium, the increase of volume of the metal, and the reducing action of the occluded gas. A. P.

**Lecture Experiments on Spectrum Analyses.** By E. CLEMINSHAW (*Phil. Mag.* [5], 19, 365—368).—The oxy-hydrogen flame supplies a ready and simple means of projecting spectra on the screen. The hydrogen is rapidly generated from zinc and hydrochloric acid in a bottle, into which strong solutions of any of the alkaline or alkaline-earth chlorides can be introduced. Or the flame may be used to ignite a lime cylinder upon different portions of which the chlorides have been melted. The reversal of the D line may be readily shown by the limelight when the sodium is burnt in a Bunsen burner, the flame of which is cooled down by a properly regulated supply of carbonic anhydride. Other arrangements for this purpose are also described. R. R.

**Useful Apparatus.** By R. ANSCHÜTZ and A. KEKULÉ (*Annalen*, 228, 301—308).—1. *A modified Glaser's Combustion Furnace.*—When platinum-black is used in the combustion of organic bodies, it is impossible to effect the complete oxidation of difficultly combustible bodies by means of the simple furnace described by Kopfer (this Journal, 1876, i, 660). Good results are obtained by the platinum-black process if a Glaser's combustion furnace is used, but in order to watch the process it is desirable to replace a portion of the earthenware tiles by sheets of mica.

2. *Air-baths for drying Substances in a Current of Air.*—Air- or water-baths are specially constructed to contain Liebig's drying tubes. Perforations in the side and top of the bath allow the drying tube to be connected with an aspirator.

3. *Apparatus for drying in a Vacuum at Higher Temperatures than that of the Atmosphere.*—The caoutchouc stopper which closes the mouth of the bell-jar has three perforations. A glass tube passes through one hole and is connected with the water-pump. The two ends of a thin leaden pipe, which is coiled in a spiral, pass through the other two holes. The substance to be dried or evaporated is placed on this spiral, and a stream of hot water is allowed to circulate through the pipe.

4. *Lecture Experiment on Flame.*—An experiment to show that the flame from an oil lamp is due to burning vapour. W. C. W.

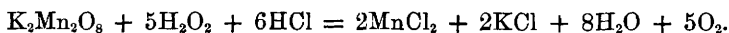
**Apparatus for Chemical Laboratories.** By D. J. WALTER (*J. pr. Chem.* [2], 31, 527—538).

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## Inorganic Chemistry.

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**Reducing Action of Hydrogen Peroxide.** By MARTINON (*Bull. Soc. Chim.*, **43**, 355—359).—If manganese dioxide is treated with hydrogen peroxide in neutral or alkaline solution, only half the quantity of oxygen is given off that would be obtained in a strongly acid solution. The same reactions take place when the oxides  $Mn_2O_3$  and  $Mn_3O_4$  are employed, although with the latter the action is much slower. When a solution of potassium permanganate is added to an acid solution of hydrogen peroxide, the following reaction takes place:—



If, however, the acid solution of hydrogen peroxide be titrated into the permanganate, a different reaction takes place, a precipitate of hydrated manganese dioxide being formed, according to the equation  $3Mn_2O_8K_2 + 9H_2O_2 + 6HCl = 6KCl + 2Mn_3O_8H_4 + 9O_2 + 8H_2O$ . This reaction varies in its character with the rate of addition of the hydrogen peroxide. On adding a neutral or alkaline solution of hydrogen peroxide to potassium permanganate, the following reaction takes place:—



If the solution of permanganate is very dilute and very alkaline, a small quantity of manganate is momentarily formed on the slow addition of the hydrogen peroxide.

Acid and alkaline or neutral solutions of hydrogen peroxide have a similar action on lead dioxide, oxygen being disengaged from both hydrogen peroxide and lead dioxide in the acid solution, whilst in the alkaline or neutral solution only half as much is disengaged, the lead dioxide being found unaltered at the end of the reaction. Mercuric oxide is only reduced in an alkaline solution, mercurous oxide being formed.

In estimating hydrogen peroxide by the author's method (this vol., p. 430), it is preferable, when a weak sample is to be assayed, to have it in acid solution, as the quantity of oxygen then evolved is double that disengaged when an alkaline solution is employed. The manganese dioxide must be free from carbonates. A. P.

**Reduction of Carbonic Anhydride to Carbonic Oxide by Carbon.** By A. NAUMANN and C. PISTOR (*Ber.*, **18**, 1647—1657).—*Water-gas*, which is obtained by the action of aqueous vapour on ignited carbon, does not consist exclusively of carbonic oxide and hydrogen, but contains also carbonic anhydride in sufficient quantity to interfere with the use of the product. The authors are making experiments with the view of ascertaining the conditions best suited to the preparation of water-gas. In this paper they describe a series of experiments in which carbonic anhydride was passed over carbon

heated to different degrees, and the amount of carbonic oxide produced ascertained. In order to determine the temperature in each experiment, salts of different melting points (enclosed in glass or platinum) were introduced between the pieces of carbon which were contained in a tube of hard glass or of porcelain; metals were used in the place of salts for the highest temperatures. The results obtained prove that (1) the lowest temperature at which the reduction of carbonic anhydride to carbonic oxide takes place is about 550; (2) the reduction increases with increased length of the layer of carbon over which the gas is passed, and diminishes with increased rapidity of current; (3) the reduction increases with the temperature.

A. K. M.

**Transformations of Sulphur.** By J. H. VAN'T HOFF (*Compt. rend.*, **100**, 1539—1540).—The author points out that many of the results described by Gernez (*Abstr.*, 1884, 889, and this vol., p. 952) have been previously obtained by L. F. Reicher and J. Ruys.

C. H. B.

**Sulphur liberated by the Decomposition of Hydrogen Persulphide.** By MAQUENNE (*Compt. rend.*, **100**, 1499—1500).—The author has previously obtained (*Bull. Soc. Chim.*, 1884, 1, 238) the nacreous variety of sulphur described by Sabatier (this vol., p. 952), by means of the same reaction, and also by adding ether to a solution of sulphur in carbon bisulphide. The nacreous crystals melt at 117°, and are rhombic prisms derived from the rhombic octahedron, and therefore do not constitute a distinct variety of sulphur.

C. H. B.

**Nacreous Crystals of Sulphur.** By D. GERNEZ (*Compt. rend.*, **100**, 1584—1585).—The nacreous crystals of sulphur recently described by Sabatier (this vol., p. 952) are not merely a modification of the octahedral variety, as Maquenne has stated (preceding Abstract), but are a distinct and unstable form, for if brought in contact with an octahedral crystal they gradually change into small transparent octahedra, which retain the general form of the original crystals.

C. H. B.

**Hydrogen Persulphide.** By P. SABATIER (*Compt. rend.*, **100**, 1585—1588).—The stability of hydrogen persulphide is increased by the presence of dissolved sulphur or hydrogen sulphide. Its decomposition is accelerated by light. Certain substances have no appreciable action on it. Amongst these are dry air, dry hydrogen, and concentrated acids. Others, including carbon bisulphide, benzene and similar hydrocarbons, paraffins, and chloroform, simply dissolve it; whilst others, such as iodine, bromine, and potassium permanganate, act on the sulphur or hydrogen sulphide dissolved by the persulphide, and thus diminish its stability. Many substances which decompose the persulphide, such as alkalis, water, alcohols, and ethers, appear to form with it highly unstable intermediate compounds.

In reply to Maquenne, the author points out that he has made no claim to the discovery of nacreous sulphur, which was first obtained by Thenard by the action of ether on hydrogen persulphide. That nacreous sulphur constitutes a distinct variety is shown by the fact

that the crystals change into octahedra and become yellow and opaque, and that if they are introduced into a cold saturated solution of sulphur in benzene they determine the formation of precisely similar nacreous crystals.

C. H. B.

**Acetic Acid and Alkaline Thiosulphates.** By E. MATHIEU-PLESSY (*Compt. rend.*, **101**, 59).—When a cold saturated solution of sodium thiosulphate is mixed with half its volume of acetic acid of 8°, only 1·5 per cent. of sulphur is precipitated, even after three or four days at 20–25°. This solution contains thiosulphuric and acetic acids in the proportion of 1 mol. to 2 mols. It yields much finer crystals than those formed from an aqueous solution of equal strength. It acts very energetically on magnesium, with development of heat and evolution of hydrogen and hydrogen sulphide, but without any greater precipitation of sulphur than would take place in the cold. It would seem that alkaline thiosulphates in presence of acetic acid have a stability sufficient to render them analogous to the corresponding sulphates.

C. H. B.

**Action of Ammonia on Solutions of Potassium Salts.** By H. GIRAUD (*Bull. Soc. Chim.*, **43**, 552–556).—On saturating a concentrated solution of potassium carbonate with ammonia, the liquid separates into two layers, the upper one containing almost all the ammonia, whilst the lower contains the potassium carbonate. On heating in a sealed tube the two liquids coalesce, but separate out again on cooling. Organic colouring matters as a rule dissolve more readily in the ammoniacal than in the potassium carbonate solution.

On adding ammonia to a solution of potassium sulphate, the salt is thrown down as a crystalline precipitate, the separation being almost complete when the solution contains 30 per cent. of ammonia.

On the addition of a saturated ammoniacal solution of sodium sulphate to an ammoniacal solution of a potassium salt, a crystalline precipitate of potassium sulphate is thrown down; the reaction is more delicate than the sodium tartrate test. Phosphoric acid must, however, be absent, as a precipitate of ammonium phosphate is formed under similar conditions. The reaction is not sufficiently delicate to permit either the titration or gravimetric estimation of potassium compounds.

A. P.

**Action of Carbonic Anhydride on Potassium Chloride in Presence of Various Amines.** By A. MULLER (*Bull. Soc. Chim.* [2], **43**, 578–583).—A continuation of the author's experiments on the rate of conversion of potassium chloride into potassium hydrogen carbonate by the passage of carbonic anhydride in the presence of ammonia. In this paper the effect of the replacement of ammonia by mono-, di-, and tri-methylamine and mono-iso-amylamine is discussed. Two series of experiments are described, in the one of which all the products remained dissolved; in the other, practically all the potassium bicarbonate and unaltered chloride were precipitated. Expressing as the coefficient of reaction the ratio of potassium chloride transformed to that taken, then in dilute solutions

trimethylamine has the lowest coefficient, but the highest velocity of carbonation; in concentrated solutions, dimethylamine has the highest coefficient, and the salts formed are the least soluble.

Of the possible reactions, the one which has the highest exothermal value is  $2\text{KCl} + 2\text{NR}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O} = 2\text{KHCO}_3 + 2\text{NR}_3\text{HCl}$ ; but the amine hydrochloride, when in solution, is in a partial state of dissociation, so that the hydrochloric acid tends to decompose the potassium hydrogen carbonate. These two reactions, *i.e.*, the formation and decomposition of the carbonate, proceed each with its own velocity; the one increasing, the other diminishing as the carbonation proceeds. Equilibrium takes place when these two velocities are equal.

V. H. V.

**Action of Anhydrous Ammoniacal Ammonium Nitrate on Metals.** By G. ARTH (*Compt. rend.*, **100**, 1588—1589).—The liquid compounds obtained by passing ammonia gas over ammonium nitrate (*Compt. rend.*, **94**, 789) dissolve metallic zinc out of contact with the air, with evolution of ammonia and formation of a white crystalline solid, which dissolves partially in water, leaving a residue of zinc oxide. The solution contains nitrites in considerable proportion and a large quantity of zinc oxide. It becomes turbid owing to separation of the latter when diluted with a large quantity of water.

Iron is dissolved in a similar manner, but copper and tin seem to be unaffected.

C. H. B.

**Action of Cadmium on Ammonium Nitrate.** By H. MORIN (*Compt. rend.*, **100**, 1497—1499).—When a saturated solution of ammonium nitrate is poured upon granulated cadmium, an energetic reaction takes place with tumultuous ebullition, and the temperature rises to  $110^\circ$ ; but there is no evolution of gas. After cooling, the liquid is filtered and allowed to evaporate over calcium chloride out of direct sunlight; it then deposits transparent rhomboidal prisms, which, when dried, do not alter on exposure to air. These crystals are decomposed by water with separation of flocculent cadmium oxide; they can, however, be crystallised from a solution of ammonia. When heated, they melt and give off ammonia, and as soon as they are completely dry, they decompose with sudden deflagration, nitrogen oxides being given off, and a residue of anhydrous cadmium oxide left. They have the composition  $\text{Cd}(\text{NO}_2)_2 \cdot \text{H}_2\text{O} + 2\text{NH}_4\text{NO}_2 + \text{CdO} \cdot 2\text{NH}_3$ , and are the first instance of a crystallised double nitrite containing ammonium nitrite. The metallic cadmium reduces the ammonium nitrate to nitrite, with formation of cadmium oxide, and the latter displaces part of the ammonia forming a double nitrite. The ammonia thus liberated dissolves a further quantity of the cadmium oxide, which remains combined with the double salt.

C. H. B.

**Didymium Compounds.** By P. T. CLÈVE (*Bull. Soc. Chim.*, **43**, 359—366).—The previous work of the author on this subject (this Journal, 1875, 340) is to some extent vitiated by the presence of samarium in the didymium compounds then described. Pure *didymium oxide*,  $\text{Di}_2\text{O}_3$ , obtained free from samarium compounds by the re-

peated fractional precipitation of a dilute solution of the nitrate, is a greyish powder, sp. gr. 7.179. The atomic weight of didymium, as determined from this compound, is 142.35. It is possible that a *peroxide*,  $\text{DiO}_2$ , may exist. *Didymium chloride*,  $\text{DiCl}_3 + 6\text{H}_2\text{O}$ , forms large deliquescent crystals, sp. gr. 2.286. The *oxychloride*,  $\text{DiOCl}$ , is a grey powder obtained by igniting the oxide in a current of chlorine, sp. gr. 5.751. The *bromide*,  $\text{DiBr}_3 + 6\text{H}_2\text{O}$ , sp. gr. 2.81, forms large, very deliquescent crystals. The *zincobromide*,  $\text{DiBr}_3 \cdot 3\text{ZnBr}_2 + 12\text{H}_2\text{O}$ , forms large tabular deliquescent crystals, and is prepared by evaporating a mixture of the solutions of the bromides of the two metals over sulphuric acid. *Didymium aurochloride*,  $\text{DiCl}_3 \cdot \text{AuCl}_3 + 10\text{H}_2\text{O}$ , sp. gr. 2.663, forms large well-formed but deliquescent crystals. The *aurobromide*,  $\text{DiBr}_3 \cdot \text{AuBr}_3 + 10\text{H}_2\text{O}$ , sp. gr. 3.304, forms large, very deliquescent, almost black crystals. The *platinochloride*,  $\text{DiCl}_3 \cdot \text{PtCl}_4 + 10\frac{1}{2}\text{H}_2\text{O}$ , sp. gr. 2.689, forms brown deliquescent prisms. The *nitrate*,  $\text{Di}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$ , sp. gr. 2.249, forms a mass of radiating deliquescent prisms. The *iodate*,  $\text{Di}(\text{IO}_3)_3 + 6\text{H}_2\text{O}$ , is an amorphous precipitate; it loses 4 mols. of water on drying at  $100^\circ$ . The *periodate*,  $\text{DiIO}_5 + 4\text{H}_2\text{O}$ , sp. gr. 3.760, is obtained by treating a salt of didymium with periodic acid, as an amorphous precipitate, which becomes crystalline on standing.

*Sulphates of didymium*: (a) the anhydrous sulphate,  $\text{Di}_2(\text{SO}_4)_3$ , sp. gr. = 3.667; (b)  $\text{Di}_2(\text{SO}_4)_3 + 5\text{H}_2\text{O}$ , forms brilliant red prisms; it takes up water rapidly from the air forming the salt (c)  $\text{Di}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$ , sp. gr. 2.829. *Didymium potassium sulphate*,  $2\text{Di}_2(\text{SO}_4)_3 \cdot 9\text{K}_2\text{SO}_4 + 3\text{H}_2\text{O}$ , is obtained as a heavy powder, on treating a cold solution of didymium acetate with potassium sulphate. *Didymium ammonium sulphate*,  $\text{DiAm}(\text{SO}_4)_2 + 4\text{H}_2\text{O}$ , sp. gr. 2.575, forms small red crystals; on heating at  $100^\circ$ , it loses 3 mols. of water; the anhydrous salt has the sp. gr. 3.080.

*Didymium selenates*: (a) the anhydrous salt,  $\text{Di}_2(\text{SeO}_4)_3$ , sp. gr. 4.442; (b) the crystalline salt,  $\text{Di}_2(\text{SeO}_4)_3 + 5\text{H}_2\text{O}$ , sp. gr. 3.681, is obtained by slow evaporation in red crystals. *Didymium potassium selenate*,  $\text{DiK}(\text{SeO}_4)_4 + 5\text{H}_2\text{O}$ , sp. gr. 3.176, is obtained in red prisms by the spontaneous evaporation at  $17^\circ$  of the solutions of the component salts; the anhydrous salt has a sp. gr. of 3.839. *Didymium ammonium selenate*,  $\text{DiAm}(\text{SeO}_4)_2 + 5\text{H}_2\text{O}$ , sp. gr. 2.959, resembles the preceding salt. *Didymium sulphite*,  $\text{Di}(\text{SO}_3)_3 + 6\text{H}_2\text{O}$ , is obtained as a precipitate on heating the sulphurous acid solution of didymium oxide.

*Selenites of didymium*: (a) the basic salt,  $(\text{Di}_2\text{O}_3)_3(\text{SeO}_2)_8 + 21\text{H}_2\text{O}$ , obtained by treating solutions of a didymium salt with sodium sulphate; (b) the acid salt,  $\text{Di}_2\text{O}_3(\text{SeO}_2)_4 + 5\text{H}_2\text{O}$ , is obtained as a crystalline precipitate on treating a solution of didymium with selenious acid.

*Didymium borate*,  $\text{DiBO}_3$ , sp. gr. 5.700, is obtained by fusing the oxide with borax. The *anhydrous metaphosphate*,  $\text{Di}_2\text{O}_3(\text{P}_2\text{O}_5)_5$ , sp. gr. 3.345, is obtained in small violet crystals on fusing didymium sulphate with metaphosphoric acid; it is insoluble in acids. The *carbonate*,  $\text{Di}_2(\text{CO}_3)_3 + 8\text{H}_2\text{O}$ , is obtained by the slow action of carbonic anhydride on a feebly ammoniacal solution of didymium nitrate,



sp. gr. 2·861. *Didymium potassium carbonate*,  $\text{DiK}(\text{CO}_3)_2 + 6\text{H}_2\text{O}$ , is obtained by treating a solution of the acetate with excess of potassium carbonate.

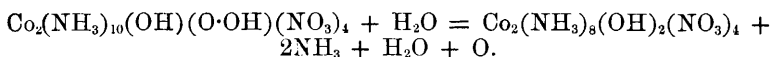
*Didymium nitroxalate*,  $\text{C}_2\text{O}_4\text{Di}_2(\text{NO}_3)_2(\text{C}_2\text{O}_4\text{H})_2 + 11\text{H}_2\text{O}$ , is obtained by slowly evaporating a solution of the oxalate in nitric acid; it forms large brilliant crystals and is a very unstable compound.

*Vanadates of didymium*: (a) orthovanadate,  $\text{DiVO}_4$ , sp. gr. 4·961, is thrown down as a fine greyish precipitate on treating ammonium metavanadate with didymium nitrate; (b) the acid salt,  $\text{Di}_2\text{O}_3(\text{V}_2\text{O}_5)_5 + 28\text{H}_2\text{O}$ , sp. gr. 2·494, is obtained on mixing solutions of sodium bivanadate and didymium nitrate.

The *formate*,  $(\text{HCO}_2)_3\text{Di}$ , sp. gr. 3·430; the *acetate*,  $(\text{MeCOO})_3\text{Di} + 4\text{H}_2\text{O}$ , sp. gr. 1·882; the *propionate*,  $(\text{EtCOO})_3\text{Di} + 3\text{H}_2\text{O}$ , sp. gr. 1·741; and the *ethyl sulphate*,  $\text{DiEt}_3(\text{SO}_4)_3 + 9\text{H}_2\text{O}$ , sp. gr. 1·863, were also prepared.

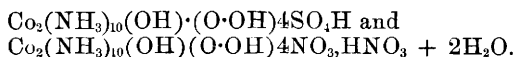
A. P.

**Cobaltammonium Compounds.** By G. VORTMANN (*Monatsh. Chem.*, **6**, 404—445).—*Oxycobaltiac salts*.—These compounds have been investigated by Fremy (*Annalen*, **83**, 227 and 289) and by Gibbs (*Amer. Acad. Arts and Sci.*, **11**, 38); they are to be considered as the first products of the action of air on ammoniacal solutions of cobalt salts. The author has prepared and analysed the nitrate, sulphate, chloride, and iodide; the method of preparation is similar to that used by Gibbs. The results of the analyses of these compounds confirm those of Fremy; the author, however, assigns to them the following constitutional formula, in which X represents a monovalent acid radicle:  $\text{HO}\cdot\text{O}\cdot\text{Co}_2(\text{NH}_3\cdot\text{NH}_3\cdot\text{NH}_3\cdot\text{X})_2(\text{NH}_3\cdot\text{NH}_3\cdot\text{X})_2\cdot\text{OH}$ . The existence of the group (O·OH), a hydrogen peroxide residue in these compounds, is shown in the reduction of potassium permanganate and dichromate by solutions of oxycobaltiac salts. Further, when heated alone, or when their ammoniacal solutions are heated, these salts lose oxygen and ammonia forming octamine salts, thus:—

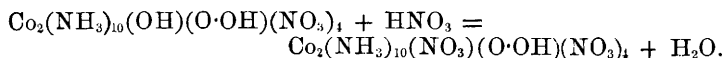


The octamine salts in turn combine with ammonia, forming decamine and luteocobaltic salts.

Oxycobaltiac salts, treated with concentrated acids, are converted into red compounds, which are acid salts, the *acid sulphate* and *nitrate* having the following composition:—



Oxycobaltiac salts, treated with dilute acids, form compounds which the author styles anhydrocobaltiac salts, the formation of which is illustrated by the following:—



These salts are decomposed by heat in a manner similar to the oxy-

cobaltiac salts, losing ammonia, water, and oxygen, and forming purplecobaltic compounds.

The following anhydro-oxycobaltiac salts have been prepared :—

Nitrate .....	$\text{Co}_2(\text{NH}_3)_{10}(\text{NO}_3) \cdot (\text{O} \cdot \text{OH}) 4\text{NO}_3 + \text{H}_2\text{O}$
Chloride .....	$\text{Co}_2(\text{NH}_3)_{10}\text{Cl} \cdot (\text{O} \cdot \text{OH}) \text{Cl}_4 + \text{H}_2\text{O}$
Chloride nitrate....	$\text{Co}_2(\text{NH}_3)_{10}\text{Cl} \cdot (\text{O} \cdot \text{OH}) \text{Cl}_3 2\text{NO}_3 + \text{H}_2\text{O}$
" .....	$\text{Co}_2(\text{NH}_3)_{10}\text{Cl} \cdot (\text{O} \cdot \text{OH}) 4\text{NO}_3 + \text{H}_2\text{O}$
Mercurchloride ....	$\text{Co}_2(\text{NH}_3)_{10}\text{Cl} \cdot (\text{O} \cdot \text{OH}) \text{Cl}_4, 3\text{HgCl}_2$
Platinochloride ....	$\text{Co}_2(\text{NH}_3)_{10}\text{Cl} \cdot (\text{O} \cdot \text{OH}) \text{Cl}_4, \text{PtCl}_4 + 5\text{H}_2\text{O}$
	$2[\text{Co}_2(\text{NH}_3)_{10} \cdot \text{O} \cdot \text{OH}] 5\text{SO}_4, 2\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$
Sulphate....	$2[\text{Co}_2(\text{NH}_3)_{10} \cdot \text{O} \cdot \text{OH}] 5\text{SO}_4, \text{H}_2\text{SO}_4 + 3\text{H}_2\text{O}$
	$2[\text{Co}_2(\text{NH}_3)_{10} \cdot \text{O} \cdot \text{OH}] 5\text{SO}_4, 8\text{H}_2\text{O}$
Chloride sulphate...	$\text{Co}_2(\text{NH}_3)_{10}\text{Cl} \cdot (\text{O} \cdot \text{OH}) 2\text{SO}_4 + 3\text{H}_2\text{O}$
Acid nitrate sulphate	$\text{Co}_2(\text{NH}_3)_{10}(\text{NO}_3) \cdot (\text{O} \cdot \text{OH}) 2\text{SO}_4, \text{H}_2\text{SO}_4$
	$+ \text{H}_2\text{O}$
Bichromate .....	$2[\text{Co}_2(\text{NH}_3)_{10} \cdot \text{O} \cdot \text{OH}] 5\text{Cr}_2\text{O}_7 + 8\text{H}_2\text{O}$
	P. P. B.

**Extraction of Zirconia and the Qualitative Composition of Zircon.** By E. LINNEMANN (*Monatsh. Chem.*, **6**, 335—347).—Zircons after treatment for several days with gaseous hydrogen fluoride can be easily reduced to a fine powder, the hydrofluoric acid dissolving out a silicate containing the following elements, Na, K, Li, Mg, Ca, Al, Fe, and Zr. After the zircon has been treated with hydrofluoric acid and extracted with water, the residue is finely powdered and heated in a silver crucible with a mixture of caustic soda and a small quantity of sodium fluoride. The fused mass is next extracted with water, and the insoluble residue, consisting of crude sodium zirconate, is treated with dilute hydrochloric acid, and the solution repeatedly evaporated to dryness. The resulting mixed chlorides are treated with a mixture of fuming hydrochloric acid (sp. gr. 1.17), absolute alcohol and ether, which leaves an insoluble residue consisting of crude zirconium chloride, which can be purified by repeatedly crystallising from hot concentrated hydrochloric acid. The qualitative examination of the chlorides soluble in alcohol, ether, &c., has shown that the following metals are associated with zirconium in the zircons :—

Sn, Pb, Cu, Bi, Al, Fe, Co, Mn, Zn, Mg, Ur, Er, Ca, Na, K, and Li.  
P. P. B.

### Mineralogical Chemistry.

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**Formation of Deposits of Nitrates in Tropical Regions.** By A. MUNTZ and V. MARCANO (*Compt. rend.*, **101**, 65—68).—In the tropical regions of South America deposits of nitrates are especially abundant in the neighbourhood of caverns, which are the homes of innumerable birds and bats, in and about which the excrement

and dead bodies of both accumulate in large quantities. In these places the formation of nitrates by the nitrification of the organic matter in contact with the calcareous rocks on which they rest can be traced step by step. The nitric acid exists in the form of calcium nitrate, which is mixed with calcium phosphate and fragments of bones.

All the deposits of nitrates in these regions contain calcium phosphate and carbonate with nitrogenous organic matter, and the presence of the latter and the calcium phosphate indicates that although the supply of animal matter has ceased, the nitrates have been derived from a source similar to that of the nitrates now in process of formation. This conclusion is further supported by the fact that the deposits frequently contain fragments of bones. Wherever the nitrates have been removed by the action of water from the place of their origin and deposited in some other locality, they are free from phosphates and recognizable animal remains. When the supply of organic matter ceases, the quantity of nitrates in the soil tends to diminish, owing to the action of rain and vegetation.

Nitrification in tropical districts is due to a microscopic organism similar to that observed by Schloesing and Muntz in temperate countries, but larger. It would seem that all the deposits of nitrates in the tropical districts of South America have had an animal origin, and have not been formed by the action of the nitrogen oxides in the atmosphere, as is frequently supposed.

C. H. B.

**Artificial Production of Strengite.** By A. DE SCHULTEN (*Compt. rend.*, **100**, 1522—1523).—When 26 c.c. of a solution of  $\text{Fe}_2\text{Cl}_6 + 12\text{Aq}$  in half its weight of water are heated with 4—5 c.c. of a solution of phosphoric acid of sp. gr. 1.578 in sealed tubes at  $180\text{--}190^\circ$  for several hours, microscopic rose-coloured crystals are obtained, which are insoluble in nitric acid, but dissolve in hydrochloric acid. If a smaller quantity of phosphoric acid is used the crystals are much smaller, whilst if the acid is in excess the yield is much smaller, or the liquid remains perfectly clear. In the latter case, if the proportion of phosphoric acid is not very large, crystals are still obtained by heating the tube to a higher temperature, which, however, must not exceed  $210^\circ$ , or a green basic phosphate is formed. When ferric hydroxide is heated with a solution of phosphoric acid in sealed tubes the product is amorphous.

The crystals have the composition of strengite,  $\text{FePO}_4 + 2\text{H}_2\text{O}$ ; sp. gr. 2.74 at  $15^\circ$ . The sp. gr. of strengite lies between 2.7 and 2.8. The artificial crystals, however, are monoclinic, whilst natural strengite is rhombic. The artificial crystals, which are highly birefractive, are frequently twinned, and in certain directions the twins yield sections closely resembling those of rhombic crystals.

C. H. B.

## Organic Chemistry.

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**Nitro-derivatives of Ethylene.** By A. VILLIERS (*Bull. Soc. Chim.*, **43**, 322—324).—The compound  $C_2K_2(NO_2)_4$ , obtained by the reduction of the potassium-derivative of tetranitroethylene bromide (Abstr., 1884, 33), undergoes decomposition after several days, forming a purplish-brown amorphous mass; potassium hydrogen carbonate is also formed, and small quantities of an unstable substance soluble in water with an intense red colour; by treating the compound  $C_2K_2(NO_2)_4$  with chlorine, bromine, or iodine in the presence of potash, tetranitroethylene chloride, bromide, or iodide is formed. The aqueous solution of the potassium compound of tetranitroethylene bromide is slowly dissociated, an oily colourless liquid being formed, which appears to be tetranitroethylene bromide. The *silver* compound,  $C_2(NO_2)_4Br_2Ag_2O$ , crystallises in brilliant yellow needles, it detonates at about  $100^\circ$ , and at  $40^\circ$  it is exploded on the slightest friction, although it cannot be exploded by friction at the ordinary temperature; it is blackened by the action of light. The *potassium* compound of tetranitroethylene chloride,  $C_2(NO_2)_4Cl_2 \cdot 2KHO$ , forms pale yellow crystals; it detonates at  $147^\circ$ . The corresponding iodine compound crystallises in yellowish plates, which alter rapidly and become black; it explodes at a higher temperature than the chlorine and bromine compounds, but causes a much more violent explosion. If in the preparation of tetranitroethylene bromide (Abstr., 1882, 815) the flask is cooled by immersing it in cold water directly the action tends to become at all violent, and the operation is then conducted as usual, the formation of nitrous gas is almost entirely avoided, and much smaller quantities of other ethylene compounds are formed. The further reduction of tetranitroethylene bromide results in its complete decomposition into ammonia, and hydrogen cyanide and bromide; a small quantity of an alkaline compound was, however, obtained by treatment with ammonium sulphide; it contained potassium and sulphur, and formed a beautiful orange platinochloride. A. P.

**Oxidation of Propylene Oxide by Silver Oxide.** By E. LINNEMANN (*Monatsh. Chem.*, **6**, 369—371).—An aqueous solution of propylene oxide reduces silver oxide with the formation of silver acetate. P. P. B.

**Volatility of Chloro-nitriles.** By L. HENRY (*Compt. rend.*, **100**, 1502—1505; compare this vol., p. 880).—The substitution of chlorine or of nitrogen for hydrogen in an organic compound is accompanied by a considerable rise in the boiling point, but if both elements are substituted in contiguous positions in one and the same molecule, the rise in the boiling point is much less marked. This effect of the contiguity of the two elements is at a maximum when they are united with the same carbon-atom, as illustrated by methane, methyl chloride, hydrogen cyanide, and cyanogen chloride. It is still evident, although

less marked, when the two substitutions take place in distinct but adjacent  $\text{CH}_3$  groups, as seen in ethane-derivatives, but it disappears altogether when the two  $\text{CH}_3$  groups are not contiguous but are separated by a  $\text{CH}_2$  group, as in the primary propane-derivatives; for example, the difference between the boiling points of  $\text{CHMe}_2\text{Cl}$  and  $\text{CH}_2\text{Me}\cdot\text{CH}_2\text{Cl}$  is only  $7-9^\circ$ , but the boiling point of  $\text{CN}\cdot\text{CHMeCl}$  is  $55^\circ$  lower than that of  $\text{CN}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ .  
C. H. B.

**Ethyl Hypochlorite.** By T. SANDMEYER (*Ber.*, **18**, 1767—1769).—The author finds that this substance is formed when gaseous hypochlorous anhydride is passed into alcohol, or when concentrated aqueous hypochlorous acid is mixed with alcohol. The most convenient method of preparation is to pass chlorine into an ice-cold solution of soda as long as it is absorbed, and immediately add, with agitation, one-tenth the volume of alcohol. The ether very soon separates, and after washing and drying with calcium chloride may be distilled. *Ethyl hypochlorite*,  $\text{ClOEt}$ , is a yellow, mobile, and very volatile liquid. It distils at  $36^\circ$  (under 752 mm. press.) undecomposed, but if the vapour be superheated a violent explosion occurs. Powdered copper (precipitated from copper sulphate with zinc) when added to the cold liquid causes a similar violent explosion. Carbon and sulphur do not act on the liquid. Ether, benzene, and chloroform do not act rapidly on this ethereal salt, but its solutions in them appear to decompose gradually. When exposed to the direct rays of the sun it explodes violently, even when the vessel containing it is surrounded with iced water. In diffused daylight, decomposition takes place more slowly, but the liquid becomes gradually warm, and after a time boils violently, and leaves only a little acid liquid smelling of ethyl acetate. In its general properties, it resembles hypochlorous anhydride very closely, and acts on ammonia and many organic substances as a strong chlorinating and oxidising agent; it immediately decomposes hydrobromic and hydriodic acids, liberating the halogens. L. T. T.

**The Wax and Fat of Cochineal.** By C. LIEBERMANN (*Ber.*, **18**, 1975—1983).—"Silver" cochineal is covered with a lustrous layer of white wax, which gives it the appearance to which it owes its name. This wax occurs also in other varieties of cochineal, the difference in appearance being probably due to the less amount of care taken in the preparation. About 2 per cent. of wax occurs on the surface of the insects, and about half as much again is obtained on finely powdering and again extracting. In addition to this wax, which differs from all previously described, and is termed coccerin, cochineal contains 4—6 per cent. of myristin and 1.5—2 per cent. of liquid fat and fatty acids which were not further investigated.

*Coccerin*,  $\text{C}_{30}\text{H}_{60}(\text{C}_{31}\text{H}_{61}\text{O}_3)_2$ , is best obtained from cochineal by extraction with boiling benzene; it crystallises in very thin plates, which collect into a characteristic satiny layer, softens at  $101^\circ$  and melts at  $160^\circ$ . It is very sparingly soluble in all cold solvents, nearly insoluble in alcohol and ether even on boiling, but soluble in hot benzene or glacial acetic acid. It is only saponified with difficulty, being converted into cocceryl alcohol and a salt of coccerylic acid. It

cannot be distilled unchanged; when heated to above  $360^{\circ}$  under 20 mm. pressure it is decomposed into coccerylic acid and an indifferent product (hydrocarbon?).

*Coccerylic acid*,  $C_{31}H_{62}O_3$ , is purified by repeated conversion into the calcium salt and crystallisation from alcohol. It forms a white crystalline powder, melts at  $92-93^{\circ}$ , is sparingly soluble in cold, but readily soluble in hot alcohol, benzene, acetic acid, ether or light petroleum. With the exception of the alkali salts, the metallic salts form flocculent precipitates, of which the calcium salt,  $(C_{31}H_{61}O_3)_2Ca$ , and barium salt,  $(C_{31}H_{61}O_3)_2Ba$ , were analysed. The ethyl salt,  $C_{31}H_{61}O_3Et$ , melts at about  $70^{\circ}$ .

*Cocceryl alcohol*,  $C_{30}H_{60}(OH)_2$ , forms a snow-white crystalline powder, melts at  $101-104^{\circ}$ , reacts vigorously with phosphoric chloride, and when heated with soda-lime at  $300^{\circ}$  is converted, with elimination of hydrogen, into an acid still under investigation.

A. J. G.

**Butenylglyceryl Chlorhydrins.** By H. ZIKES (*Monatsh. Chem.*, **6**, 348—355).—The *monochlorhydrin*,  $C_4H_9O_2Cl$ , is obtained by saturating the butenylglycerol described by Lieben and Zeisel (*Abstr.*, 1881, 711) with hydrogen chloride at  $100^{\circ}$ , and heating the resultant liquid in sealed tubes at  $100^{\circ}$ . It is an oily, colourless liquid, of sweet taste and aromatic odour; it boils at  $134-136^{\circ}$  (corr.) under 28 mm., and has a sp. gr. 1.2324 at  $17^{\circ}$ . It is soluble in water and miscible with alcohol and ether.

The *epichlorhydrin*,  $C_4H_7OCl$ , is prepared by saturating a mixture of equal volumes of glacial acetic acid and butenylglycerol with hydrogen chloride at  $100^{\circ}$ . The resulting liquid when fractionated under reduced pressure yields a portion boiling at  $100-118^{\circ}$  under 26 mm., which when heated with soda yields the epichlorhydrin, a liquid boiling at  $125.5^{\circ}$  (corr.) under 738 mm., and of sp. gr. 1.098 at  $15^{\circ}$  (water at  $15^{\circ} = 1$ ). When treated with hydrogen chloride, it forms the *dichlorhydrin*,  $C_4H_7OCl_2$ , an oily colourless liquid, having an aromatic odour, and boiling at  $105-107^{\circ}$  under 30 mm. pressure. It is sparingly soluble in water, but easily miscible with alcohol and ether. Its sp. gr. is 1.274 at  $16^{\circ}$  (water at  $16^{\circ} = 1$ ).

P. P. B.

**Reduction of Hexahydric Alcohols.** By J. A. LE BEL and M. WASSERMANN (*Compt. rend.*, **100**, 1589—1591).—The secondary iodide obtained from the alcohol by Wanklyn and Erlenmeyer's reaction is placed in a hydrogen apparatus containing zinc and hydrochloric acid, and the evolved gas is passed through heavy petroleum which dissolves the more volatile hydrocarbon formed by the reduction. The latter is isolated by heating the hydrogen apparatus and the heavy hydrocarbon, and practically the theoretical yield is obtained.

The hydrocarbon obtained in this way from the iodide obtained from mannitol boils at  $68-69^{\circ}$ , and is a normal paraffin.

C. H. B.

**Raffinose.** By C. SCHEIBLER (*Ber.*, **18**, 1779—1786).—In continuation of his previous work (this vol., p. 962) the author has carefully compared this sugar with the gossypose obtained by Böhm

and Ritthausen from cotton-seed cake, and finds them to be identical. Loiseau (this Journal, 1876, ii, 397) proposed the formula  $C_{18}H_{32}O_{16} + 5H_2O$  for raffinose, whilst Ritthausen gave the formula  $C_{12}H_{22}O_{11} + 3H_2O$  to his sugar (from cotton-seed cake), which he considered to be mellitose. The determination of the water of crystallisation has not hitherto been successfully made, as when simply dried by heating no constant weight is obtained below  $120^\circ$ , at which temperature the sugar begins to turn yellow, and its solution then reduces Fehling's solution. But by first drying the sugar for 14—16 days over sulphuric acid at the ordinary temperature (during which about 13 per cent. of water was usually lost), and then heating in the water oven, the author succeeded in obtaining constant weights without any decomposition. The sugars obtained from each of the above-named sources gave numbers which proved the correctness of Loiseau's formula,  $C_{18}H_{32}O_{16} + 5H_2O$ . The rotations also agreed, giving  $[\alpha]_D = +103.9$ — $103.4$ , or  $[\alpha]_j = +114.6$ . Loiseau found  $[\alpha]_D +105.5$ , and Tollens (this vol., p. 368)  $+102.5$  for raffinose, and Ritthausen  $+104.4$  for gossypose. When inverted by means of sulphuric acid, both sugars gave identical results. A 10 per cent. solution kept with 2 per cent. sulphuric acid at about  $17$ — $18^\circ$ , gave at first a rapidly decreasing rotation: after about ten days the rotation became constant, and gave  $[\alpha]_D = 52.3$ . When the inversion was carried out at  $60^\circ$ , the above diminution in rotation was reached in about three and a half hours, and a further gradual diminution took place, until after 20 hours the rotation gave  $[\alpha]_D = 45.2$ . But by this time, the sugar solution had become discoloured, and the author believes the first to be the correct number for the invert-sugar, and the latter only due to decomposition. No crystallisable sugar could be obtained from the inverted solution.

The author believes that the raffinose is present in the beetroot, and not formed during the storage period or refining process—as Loiseau, from giving it the name *raffinose*, would appear to have believed. The author believes the presence of raffinose to account for the high rotation of many crude sugars—a rotation which is often observed to diminish by storage. For, as already seen, raffinose is not so stable as cane-sugar, and is partly inverted even by heating at  $100^\circ$ . He therefore cautions beet-growers against striving too much towards obtaining beets giving such highly polarising juices without first ascertaining that the high degree of polarisation is not brought about by the development in the sap of an increased percentage of raffinose rather than of sugar. Many commercial sugars which do not reduce Fehling's solution lose a very high percentage of water when dried at  $100^\circ$ , become discoloured, and their solution then reduces Fehling's solution to a considerable extent. The author believes this action to be due to the presence of raffinose, and to be a valuable qualitative test of such presence. The author hopes shortly to subject mellitose to a similar investigation in order to ascertain whether it really is different from raffinose or not.

L. T. T.

**Alkaloids Produced by the Action of Ammonia on Glucose.**  
By C. TANRET (*Compt. rend.*, 100, 1540—1543).—60 parts of glucose



were heated with 100 parts of ammonia of 25° in sealed tubes at 100° for 30—40 hours. The blackish syrup thus obtained contains ammonium carbonate, a nitrogenous derivative described by P. Thénard, free ammonia, formic acid, and about 1·5 per cent. of alkaloids. To isolate the latter, the liquid is agitated with chloroform and the latter with dilute sulphuric acid, the crude products being further separated by fractional distillation.

The products are  $\alpha$ -glucosine,  $C_6H_8N_2$ , which boils at 136°; sp. gr. at 0° = 1·038; vapour-density, 3·81; and  $\beta$ -glucosine,  $C_7H_{10}N_2$ , which boils at 160°; sp. gr. at 0° = 1·012; vapour-density, 3·87. Both the glucosines are colourless, very mobile, highly refractive, volatile liquids, with a powerful and peculiar odour. In acid solutions, they give precipitates with the ordinary reagents for alkaloids. They have a feebly alkaline reaction, and, like caffeine, narcotine, and other weak bases, are removed from acid solutions by chloroform. They do not precipitate metallic oxides, but produce colour changes in solutions of copper and iron, and give a precipitate with mercuric chloride. When treated with dry hydrogen chloride, they form crystallised deliquescent hydrochlorides. With gold chloride, they give canary-yellow precipitates of the composition  $C_6H_8N_2 \cdot AuCl_3$  and  $C_7H_{10}N_2 \cdot AuCl_3$  respectively, and with platinic chloride they yield precipitates which form slowly and the composition of which has not yet been determined. In warm solutions, a platinichloride seems to be formed, as in the case of pyridine bases. The glucosines combine with warm ethyl iodide to form blackish non-crystallisable products which when decomposed by potash yield a highly basic, extremely unstable alkaloid, the composition of which could not be determined. In the cold, the glucosines and ethyl iodide combine more slowly in the proportion of equal molecules. When heated in sealed tubes at 100° with hydrochloric acid or potash solution, they yield no ammonia, and when treated with sodium hypobromite no nitrogen is evolved. It would seem, therefore, that the glucosines are not amides. They are not affected by nitrous acid, chromic acid, or mercuric oxide, but are oxidised by potassium permanganate in presence of sulphuric acid with evolution of carbonic anhydride and formation of ammonium sulphate. They are violently decomposed by nitric acid with formation of nitrogen oxides, carbonic anhydride, hydrocyanic acid, and oxalic acid. When brought in contact with sodium, they become dark-coloured, and seem to resinify, but no gas is given off.

Alkaloidal substances are also produced by the action of compound ammonias and some of their salts on glucose. C. H. B.

**Action of Oxidising Agents on Chloral Hydrate.** By S. COTTON (*Bull. Soc. Chim.*, 43, 420—423).—The yellow variety of mercuric oxide decomposes an aqueous solution of chloral hydrate, forming carbonic anhydride, carbonic oxide, and mercuric oxychloride. Red mercuric oxide acts in the same way, but is less active than the yellow variety.

Potassium permanganate acts on chloral hydrate in two distinct stages: in the first, potassium manganate and manganese dioxide are formed, part of the chloral hydrate being completely decomposed,

and carbonic anhydride, oxygen and chlorine are disengaged; whilst in the second stage the potassium manganate reacts upon a further amount of chloral hydrate with formation of chloroform and evolution of oxygen and carbonic anhydride.

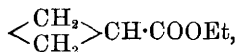
Chromic acid acts violently on crystals of chloral hydrate, carbonic anhydride and carbonic oxide being formed: in dilute aqueous solution in the cold, it does not attack the chloral hydrate, but reaction takes place on warming.

Chromic acid and potassium permanganate have practically no action on chloroform, bromoform, or iodoform; yellow mercuric oxide also appears to be quite without action on either chloroform or bromoform; it acts rapidly, however, on iodoform, carbonic oxide, containing traces of carbonic anhydride, being given off. A. P.

**Oxidation of Oleic Acid by an Alkaline Solution of Potassium Permanganate.** By A. SAYTZEFF (*J. pr. Chem.* [2], **31**, 541—542).—By the oxidation of oleic acid, an acid is obtained crystallising in rhombic leaflets, melting at  $136.5^{\circ}$  and of the formula  $C_{18}H_{36}O_4$ : with phosphorous iodide, it yields moniodostearic acid, and is identical with the dihydroxystearic acid obtained by Overbeck from dibromoleic acid. J. K. C.

**Diammonium Chloride.** By R. ANSCHÜTZ and C. HINTZE (*Ber.*, **18**, 1394—1397).—The authors have obtained crystals of ammonium oxalate, some showing right- and some left-handed hemihedrisms similar to that observed on the crystals of ammonium sodium dextro- and lævo-tartrate obtained by recrystallising ammonium sodium racemate. So far, however, they have not been able to observe any difference in chemical behaviour between the right- and left-handed crystals. A. J. G.

**Trimethylenedicarboxylic Acid.** By W. H. PERKIN, jun. (*Ber.*, **18**, 1734—1738).—Diethyl malonate may be converted into diethylic diethylmalonate by treatment with sodium ethoxide and ethyl iodide; this being a general method for the formation of ethereal salts of the doubly-substituted malonic acids from malonic acid and all its known derivatives; but trimethylenedicarboxylic acid does not yield this reaction, and therefore cannot be considered as vinylmalonic acid (this vol., p. 853). Further, *ethyl trimethylenemonocarboxylate*,



which forms a colourless oil boiling at  $133^{\circ}$  to  $134^{\circ}$ , is only acted on by bromine with the greatest difficulty, and is quite unaffected by hydrogen bromide—facts which cannot well be reconciled with the formula  $COOEt \cdot CH_2 \cdot CH : CH_2$ . A. P.

**Malic Acids.** By R. ANSCHÜTZ (*Ber.*, **18**, 1949—1953).—Inactive malic acid has been prepared from six sources, namely, (1) from inactive aspartic acid, (2) from monobromosuccinic acid, (3) from fumaric acid and water, (4) from ethyl dichloropropionate with potas-

sium cyanide, (5) from fumaric acid with aqueous soda, and (6) from racemic acid; the question as to the identity of these acids is, however, still open. In the present communication it is shown by the crystallographic examination of the hydrogen ammonium salt prepared from the second and third sources that these acids are identical with that from the first, and Werigo and Tanatar have shown that the acids from the first and fourth sources are identical. The author hopes soon to be able to speak positively as to the nature of the acids from the fifth and sixth sources.

The following salts of malic acid were prepared by passing a current of hydrogen chloride into strongly cooled solutions of malic acid in the respective alcohols; the formation of fumarates or of monochlorosuccinates being avoided by this means. Under 10 mm. pressure the methyl salt boils at 122°, the ethyl salt at 128°, the propyl salt at 151°. When treated with acetic chloride these compounds are converted into the corresponding salts of acetomalic acid; the methyl salt boils at 129° under 11 mm. pressure, the ethyl salt at 137° under 10 mm. pressure, the propyl salt at 157° under 12 mm. pressure.

A. J. G.

**Preparation of Aconitic Acid from Citric Acid.** By R. ANSCHÜTZ and F. KLINGEMANN (*Ber.*, 18, 1953—1955).—Aconitic acid can be prepared from citric acid by heating, or by the action of hydrogen chloride at 140°. In either case, the purification of the acid presents considerable difficulties. Pure aconitic acid is, however, readily prepared by converting the citric acid into a normal ethereal salt, and gently heating this with acetic chloride, when the acetylcitrate is obtained; this, when heated at 250—280°, yields acetic acid and a normal aconitate. This is converted into aconitic acid by heating for some time in a reflux apparatus with excess of hydrochloric acid.

*Trimethyl citrate* boils at 176° under 16 mm. pressure; the *ethyl* salt boils at 185° under 17 mm. pressure; the *propyl* salt boils at 198° under 13 mm. pressure.

*Trimethyl acetylcitrate* boils at 171°, and the *ethyl* salt at 197° under 15 mm. pressure; the *propyl* salt boils at 205° under 13 mm. pressure.

*Trimethyl aconitate* boils at 161°, and the *ethyl* salt at 171° under 14 mm. pressure; the *propyl* salt boils at 195° under 13 mm. pressure.

A. J. G.

**Artificial Uric and Methyluric Acids.** By J. HORBACZEWSKI (*Monatsh. Chem.*, 6, 356—362).—This paper contains an account of the author's further experiments on the synthesis of uric acid (*Abstr.*, 1883, 179). This synthesis is most easily effected by carefully heating small quantities of glycocine (0.1—0.2 gram) with 10 to 15 times its weight of urea, until a considerable quantity of precipitate has been formed in the molten mass. The uric acid is separated from the product in the manner already described (*loc. cit.*); the crude mass itself exhibits the reactions of uric acid. *Methyluric acid* is obtained in a similar manner by heating small quantities of sarcosine with 5 to 10 times its weight of urea. The methyluric acid is isolated in a manner similar to that adopted in the case of uric acid;

it is apparently identical with that obtained by Hill from lead urate and methyl iodide. The yield in both cases is small. P. P. B.

**The Thiophen Group.** By V. MEYER (*Ber.*, **18**, 1770—1773).—Since Volhard and Erdmann obtained a third thiotolen (this vol., p. 763)—whereas the hitherto received thiophen formula only allows the possibility of two monomethylthiophens—the author has, in conjunction with his students, again taken up the study of this group, and now gives some of the preliminary results obtained. Muhlert has re-examined Volhard and Erdmann's thiotolen. When oxidised, it yields a crystalline thiophenic acid which melts at  $136^{\circ}$  (the known isomerides melt at  $118^{\circ}$  and  $126.5^{\circ}$ ); it is volatile in steam, gives a blue coloration with isatin and sulphuric acid, and also shows Laubenheim's reaction, but the colour produced is blue instead of red or violet.

Pendleton, by distilling pure  $\beta$ -thiophenic acid with potassium cyanide has obtained an isomeric acid which differs entirely in properties from the  $\beta$ -acid.

Schleicher has found that the monobromothiophen obtained as a bye-product in the preparation of dibromothiophen is a  $\beta$ -derivative.

Ahrens has found that when ethyl selenide is passed through red-hot tubes a substance is produced which closely resembles thiophen, gives the Laubenheim reaction, and forms bromo-substitution derivatives.

Professor Marmé finds that nitrothiophen is a very violent poison, and when given to rabbits, even in very small quantities, causes death, accompanied by the chocolate coloration of the blood characteristic of poisoning by nitrobenzene. L. T. T.

**Tribromothiophen and Double Compounds of Dinitrothiophen.** By J. ROSENBERG (*Ber.*, **18**, 1773—1778).—By treating 5 grams of dibromothiophen with 3.3 grams of bromine (equal molecular proportions), the author succeeded in obtaining *tribromothiophen*,  $C_4SHBr_3$ . It crystallises in needles or spiculæ, melts at  $29^{\circ}$ , and boils at  $259$ — $260^{\circ}$  (corr.). It is sparingly soluble in cold alcohol, easily so in ether and boiling alcohol. When treated with pyrosulphuric acid (6 grams of pure bromo-compound with 5 grams melted acid), it yields *tribromothiophensulphonic anhydride*,  $(C_4SBr_3SO_3)_2O$ . This anhydride melts at  $115$ — $116^{\circ}$ , and is easily soluble in alcohol and ether, sparingly so in boiling water. It is volatile with steam, being at the same time partially hydrated to the acid. It is converted into *tribromothiophensulphonic acid* when boiled with potash or soda, more easily so by barium hydroxide, yielding with the latter the crystalline salt,  $(C_4SBr_3SO_3)_2Ba + H_2O$ . When debrominated, it yields  $\beta$ -thiophensulphonic acid. If the sulphonation of the tribromothiophen is not carried out very carefully and the mixture kept cool, the sulphonic groups often displace the bromine. In one instance, a *thiophentrisulphonic acid* was obtained, the chloride of which melted at  $79$ — $80^{\circ}$ .

When a mixture of molecular proportions of naphthalene and dinitrothiophen is dissolved in benzene, and the solution allowed to evaporate spontaneously, a double compound,  $C_{10}H_8 + C_4SH_2(NO_2)_2$ , crystallises out in long yellow needles, melting at  $50^{\circ}$ . With anthra-

cene a similar compound,  $C_{14}H_{10} + C_4SH_2(NO_2)_2$ , is obtained, which crystallises in scales melting at  $162^\circ$ . L. T. T.

**Thioxylen from Coal-tar.** By J. MESSINGER (*Ber.*, **18**, 1636—1640).—The author gives the following method of isolating pure thioxylen, which is preferable to that previously described (this vol., p. 767). After obtaining the iodo-product, this is dissolved in cold alcoholic soda solution, zinc-dust added, and the mixture heated for an hour on a water-bath. It is then distilled in a current of steam until the distillate becomes turbid, a large bulk of water added to the distillate, and then a saturated solution of calcium chloride, which causes the thioxylen to separate. A shorter way is to filter the reduced product from the zinc-dust, which is then washed with alcohol, and the filtrate acidified with dilute hydrochloric acid, when the thioxylen separates nearly quantitatively. In fractioning large quantities of thioxylen, a small quantity of a higher boiling substance has been observed, which may perhaps be a higher homologue of thioxylen. The sp. gr. of thioxylen is  $0.9755$  at  $17.5^\circ$  compared with water at the same temperature.

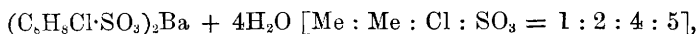
*Monobromothioxylen*,  $C_4SHMe_2Br$ , may be readily obtained by brominating pure thioxylen diluted with carbon bisulphide; after purification, it forms a colourless liquid, heavier than water, and boiling at  $193$ — $194^\circ$  (uncorr.). *Moniodothioxylen*,  $C_4SHMe_2I$ , forms a mobile colourless liquid, which darkens on exposure to light; it cannot be distilled without decomposition. *Mononitrothioxylen*,  $C_6H_7S \cdot NO_2$ , is formed on passing air saturated with thioxylen vapour through a mixture of fuming nitric and glacial acetic acids; it is a heavy yellow liquid having an odour recalling that of nitrobenzene, and is not volatile without decomposition. When a drop of dilute potash is added to a dilute alcoholic solution of nitrothioxylen, a reddish-violet coloration is produced, which, however, may perhaps be due to the presence of a trace of dinitrothioxylen.

*Methyl thiophendicarboxylate*, which was previously described (this vol., p. 767), is found to melt somewhat higher (namely at  $145^\circ$ ) than was then stated. The *ethyl salt* forms beautiful long needles melting at  $46^\circ$ . The author's thiophendicarboxylic acid, obtained by the oxidation of thioxylen, is found to be identical with Jackel's acid, which was prepared from thiophendisulphonic acid. A. K. M.

**Monochlorometaxylene.** By O. JACOBSEN (*Ber.*, **18**, 1760—1762).—Pure metaxylenesulphonamide, melting at  $138$ — $139^\circ$ , was heated at  $200^\circ$  with hydrochloric acid, and the pure metaxylene thus obtained (after the addition of 5 per cent. of iodine) was chlorinated at  $0^\circ$ . The product was purified by converting it into its sulphonic acid. This acid when converted into the barium salt proved to be perfectly homogeneous. *Monochlorometaxylene*,  $C_6H_3Me_2Cl$  [1 : 3 : 4] boils at  $186.5^\circ$  (col. in vapour), under 767 mm. pressure, and is still liquid at  $-20^\circ$ . Its sp. gr. is  $1.0598$  at  $20^\circ$  (water at  $20^\circ$ ). When oxidised by chromic mixture, it yielded Vollrath's acid,  $C_6H_3Me_2Cl \cdot COOH$  [ $COOH$  : Me : Cl = 1 : 3 : 4], the correct melting point of which is  $209$ — $210^\circ$  (corr.), and not  $204^\circ$ . The constitution of the sulphonic acid [Me : Me : Cl :  $SO_3H$  =

1 : 3 : 4 : 6] was proved by the elimination of the Cl by sodium amalgam. It forms a sulphonamide, crystallising in hard glittering prisms which melt at  $195^{\circ}$ .  
L. T. T.

**Monochloro-xylenes and their Oxidation-products.** By A. KRÜGER (*Ber.*, 18, 1755—1760).—Five per cent. of iodine was added to ice-cold orthoxylene and chlorine then passed in until the increase of weight represented the formation of a monochlorinated derivative. Two isomeric compounds were formed, which were separated by means of the barium salts of their mono-sulphonic acids. Each chloro-derivative formed only one sulphonic acid. *Monochloro-ortho-xylene*,  $C_6H_3Me_2Cl$  [Me : Me : Cl = 1 : 2 : 3] was obtained from the sparingly soluble barium salt,  $(C_6H_3ClSO_3)_2Ba + H_2O$  [Me : Me : Cl :  $SO_3$  = 1 : 2 : 3 : 6], which separated as a crystalline film from the boiling solution. This chloro-xylene boils at  $189.5^{\circ}$  (corr.), and does not solidify at  $-20^{\circ}$ . The more soluble barium sulphonate,



which crystallised in long needles, yielded *monochloro-ortho-xylene*,  $C_6H_3Me_2Cl$  [1 : 2 : 4], boiling at  $191.5^{\circ}$ , and remaining liquid at  $-20^{\circ}$ ; its sp. gr. is 1.0692 at  $15^{\circ}$  (water at  $15^{\circ}$ ). The *potassium*, *sodium*, and *barium* salts, and the amides of both sulphonic acids are described. Both chloro-xylenes were oxidised with dilute nitric acid, sp. gr. 1.19—1.20, and the constitution of the resulting toluic acids proved by their conversion into known compounds by fusion with potash. The 1 : 2 : 4 chloro-xylene yielded the acid  $C_6H_3MeClCOOH$  [Me :  $COOH$  : Cl = 1 : 2 : 4], crystallising in needles, melting at  $166^{\circ}$ , and the isomeric acid,  $COOH$  : Me : Cl = 1 : 2 : 4, crystallising in prisms or needles melting at  $130^{\circ}$ . The 1 : 2 : 3 chloroxylylene yielded only the acid  $COOH$  : Me : Cl = 1 : 2 : 3, which crystallised in needles melting at  $154^{\circ}$ . The *calcium* salts of these acids are described. The toluic acids when treated with alkaline permanganate yielded their corresponding chlorophthalic acids. The acid  $C_6H_3Cl(COOH)_2$  [ $COOH$  :  $COOH$  : Cl = 1 : 2 : 4] is easily soluble in alcohol and water, crystallises in silky needles, and melts at  $130$ — $134^{\circ}$ . On distillation, it yields an anhydride which melts at  $95^{\circ}$ , identical with that obtained by Alén (*Abstr.*, 1882, 409) from *ε*-dichloronaphthalene. The 1 : 2 : 3 acid is less soluble; it melts at  $179$ — $181^{\circ}$ , and when distilled gives an anhydride melting at  $122^{\circ}$ . Both acids when fused with potash yielded the hydroxyphthalic acid,  $COOH$  :  $COOH$  :  $OH$  = 1 : 2 : 4, a result probably due, in the case of the 1 : 2 : 3 acid, to a migration of the carboxyl-group at the high temperature of the fusion. The constitution of the sulphonic acids was proved by eliminating the chlorine by means of sodium amalgam. The one yielded the known acid 1 : 2 : 4, melting at  $144^{\circ}$ , whereas the sulphonic acid from the 1 : 2 : 3 chloroxylylene yielded an orthoxylenesulphonic acid, Me : Me :  $SO_3H$  = 1 : 2 : 3 (or 1 : 2 : 6), which gave a crystalline amide melting at  $165^{\circ}$ .  
L. T. T.

**Oxidation-products of Solid /Dibromoparaxylylene.** By B. SCHULTZ (*Ber.*, 18, 1762—1763).—Dibromoparaxylylene,  $C_6H_2Br_2Me_2$

[Me : Br : Me : Br = 1 : 3 : 4 : 6] when treated with chromic acid in acetic solution, yields *dibromoparatoluic acid*,  $C_6H_2MeBr_2.COOH$  [COOH : Br : Me : Br = 1 : 3 : 4 : 6]. This acid is soluble in alcohol, sparingly so in boiling water, crystallises in stellate needles, and melts at  $195^\circ$ . Its *ethyl salt* forms long needles, which are soluble in alcohol, melt at  $49^\circ$ , and boil at  $310^\circ$ . The *barium* and *calcium salts* form needles, sparingly soluble in water. The acid, when oxidised with alkaline permanganate, yields Claus and Wimmel's *dibromoterephthalic acid*,  $C_6H_2Br_2(COOH)_2$  (Abstr., 1880, 632). The *ethyl salt* of this latter acid forms micaceous scales, which melt at  $125^\circ$  and boil at  $335^\circ$ ; the *barium* and *calcium salts* form minute, easily soluble needles.

L. T. T.

**Aromatic Hydrocarbons.** By R. D. SILVA (*Bull. Soc. Chim.*, **43**, 317—322).—*Isopropylbenzene*,  $C_6H_5Pr^i$ , may be prepared by acting on benzene with normal or iso-propyl chloride; it may also be prepared in an indirect manner by acting on benzene with allyl chloride, as also by the action of dichloroacetol on benzene. It is a colourless, very mobile liquid, of pleasant odour; boils at  $151$ — $152^\circ$ , and has a sp. gr. of 0.8776 at  $0^\circ$ , and 0.8577 at  $25^\circ$ .

*Diisopropylbenzene*,  $C_6H_4Pr_2^i$ , obtained as a secondary product of the action of isopropyl chloride on benzene, is a colourless liquid, similar in odour to isopropylbenzene, and boils at about  $202^\circ$  under 759 mm. pressure. When normal instead of isopropyl chloride is employed, a liquid boiling at about  $206^\circ$  under 759 mm. pressure is obtained, which is very similar in all respects to the preceding compound; the author is, however, unable to say whether the products are identical.

*Isopropyltoluene*,  $C_6H_4MePr^i$ , is obtained by the action of isopropyl chloride on toluene in presence of aluminium chloride. It is a colourless, refractive liquid, its odour resembles that of the cymene obtained from camphor. It boils at  $172$ — $173^\circ$  under the ordinary pressure, and has a sp. gr. of 0.86948 at  $0^\circ$ , and 0.86211 at  $25^\circ$ . A second cymene is obtained by the action of normal propyl chloride on toluene in the presence of aluminium chloride; it is a colourless refractive liquid, having an agreeable odour, but quite unlike that of isopropyltoluene; it boils at  $180$ — $182^\circ$ .

A. P.

**Phosphates of the Phenols.** By E. KREYSLER (*Ber.*, **18**, 1700—1706).—The following normal phosphates of the aromatic series are obtained by heating phosphoric oxychloride with excess of the corresponding phenols; the yield is about 80 per cent. of the theoretical amount.

*Tri-isobutylphenyl phosphate*,  $(C_4H_9-C_6H_4)_3PO_4$ , is obtained as a yellowish viscous oil, having a slight aromatic odour; it cannot be solidified by cooling with ice and salt. It boils above  $400^\circ$  with partial decomposition, and is readily soluble in the usual solvents, with the exception of cold alcohol and petroleum.

*Tri-isoamylphenyl phosphate*,  $(C_5H_{11}-C_6H_4)_3PO_4$ , has similar properties to the above; it boils with partial decomposition above  $400^\circ$ , and may be distilled unaltered in a vacuum.

*Triortho-xytyl phosphate*,  $(C_6H_3Me_2)_3PO_4$ , is a yellowish oil, having a

slight greenish fluorescence and aromatic odour; it may be distilled unaltered in a vacuum. It does not solidify on cooling.

*Trimetaxylyl phosphate* forms, when freshly prepared, a clear yellow oil; after a time it becomes turbid, and is partially decomposed; it distils unaltered under 200 mm. pressure.

*Tricarvacryl phosphate*,  $(C_{10}H_{13})_3PO_4$ , is readily obtained in lustrous monoclinic prisms or tablets. It melts at  $75^\circ$ , and may be distilled unaltered in a vacuum; the crystals show phosphorescence on rubbing in the dark. Trithymyl phosphate, already obtained by Englehart and Latschinoff (*Zeit. f. Chem.*, 1869, 44), forms a light yellow oil, which crystallises after a time, forming colourless needles; it melts at  $59^\circ$ . In spite of the excess of thymol used in preparing this compound, some *monochlorodithymyl phosphate* was formed, from which by treatment with aqueous soda *sodium dithymylphosphate*,  $(C_{10}H_{13})_2NaPO_4$  was obtained in white felted needles; it melts at  $74^\circ$ , and by heating is converted, with partial carbonisation, into trithymyl phosphate. A. P.

**Reactions of the Phosphates of the Aromatic Series.** By E. KREYSLER (*Ber.*, 18, 1706—1723).—By heating the aromatic phosphates with potassium cyanide, the corresponding nitriles are obtained; the yield of the pure substance is between 15 and 20 per cent. of the phosphate employed.

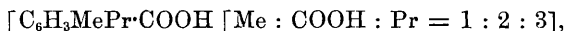
*Paraisobutylbenzonitrile* forms a pale yellowish oil, which is converted into *paraisobutylbenzoic acid*,  $C_4H_9 \cdot C_6H_4 \cdot COOH$ , when heated with alcoholic potash, &c.; this may be sublimed in colourless feathery needles, and melts at  $160$ — $161^\circ$ .

*Isoamylbenzonitrile*,  $C_5H_{11} \cdot C_6H_4 \cdot CN$ , forms a colourless aromatic oil, boils at  $260$ — $263^\circ$  (uncorr.), and does not solidify when cooled with a mixture of ice and salt; on heating it with alcoholic potash, *para-isobutylbenzoic acid*,  $C_5H_{11} \cdot C_6H_4 \cdot COOH$ , is formed. This sublimes in colourless needles, melts at  $158^\circ$ , and is soluble in the usual solvents, with the exception of cold water; the *silver salt*,  $C_5H_{11} \cdot C_6H_4 \cdot COOAg$ , crystallises in small colourless needles.

*Ortho-xylonitrile*,  $C_6H_3Me_2CN$ , is obtained as a colourless mobile oil, having an odour like that of benzaldehyde; it boils at  $230$ — $232^\circ$ , and is converted by the action of alcoholic potash into *ortho-xylic acid*.

*Metaxylo-nitrile* is obtained as a colourless aromatic oily liquid, boiling at  $221$ — $224^\circ$ , and is converted into *metaxylic acid* by the action of alcoholic potash.

*Carvacronitrile*,  $C_6H_3MePr \cdot CN$ , is obtained as a colourless oily liquid of an agreeable odour; it boils at  $244$ — $246^\circ$ ; by the action of alcoholic potash, it is converted into *parapropylorthotoluic acid*,



this crystallises in white needles, is almost insoluble in cold water, but is readily soluble in hot water, alcohol, and ether; it melts at  $75^\circ$ ; the *silver salt*,  $C_6H_3MePr \cdot COOAg$ , was also prepared.

On distilling triphenyl phosphate with sodium acetate or benzoate, phenyl acetate or benzoate are respectively formed. On distilling triisobutylphenyl phosphate with sodium benzoate, isobutylphenyl



benzoate is formed. Isoamylphenyl benzoate is obtained in a similar way from the corresponding phosphate.

On heating triphenyl phosphate with potassium sulphide, *triphenyl thiophosphate*,  $\text{Ph}_3\text{PSO}_3$ , is obtained in silky colourless needles; it melts at 48–49°.

On distilling triphenyl phosphate with magnesia, phenol and a small quantity (3 per cent.) of diphenylene oxide and diphenyl oxide are formed; whilst on distilling with calcium, zinc, or lead oxide, phenol and diphenylene oxides only are formed. A. P.

**Silicates of the Phenols.** By J. HERTKORN (*Ber.*, 18, 1679–1699).—*Tetraphenyl silicate*,  $\text{Ph}_4\text{SiO}_4$ , is prepared by the action of silicon tetrachloride in the absence of water on excess of pure phenol; the yield is good, about 78 per cent. of the theoretical amount; it boils at 417–420°; on cooling to 0°, it forms a thick syrup, which on shaking or stirring crystallises in long colourless prisms; it melts at 47–48°, has no odour, and is readily soluble in dry benzene, ether, alcohol, carbon bisulphide, chloroform, &c. Cold water slowly decomposes it into phenol and silicic acid. On heating phenyl silicate with dry ethyl alcohol, phenol and tetrethyl silicate are obtained; on heating it with boric anhydride, a phenyl borate, an acid phenyl silicate, and probably silicic acid are formed. A solution of tetraphenyl silicate in glacial acetic acid deposits a white flocculent precipitate, especially when heated. When tetraphenyl silicate was heated with freshly ignited magnesium oxide, phenol was obtained, but not, as was expected, diphenyl oxide. When heated with potassium cyanide or ferrocyanide, phenol was also obtained, together with traces of phenyl cyanide. The following silicates were likewise obtained from their corresponding phenols in a similar manner to the preceding; the yield is always good, being between 75 and 90 per cent. of the theoretical; their solubilities and general reactions are also similar to those of the phenyl compound.

*Tetrorthocresyl silicate*,  $(\text{C}_6\text{H}_4\text{Me})_4\text{SiO}_4$ , is a colourless mobile liquid boiling at 435–438°; it becomes feebly dichroic by the action of light; it may be obtained in the crystalline form by dissolving in benzene, cooling, and evaporating in a vacuum over sulphuric acid.

*Tetrametacresyl silicate* forms a slightly yellowish syrupy liquid, and boils at 443–446° under 720 mm. pressure.

*Tetraparacresyl silicate* is a colourless syrup which by cooling may be obtained in colourless prismatic crystals; it melts at 69–70°, and boils at 442–445°.

*Tetrametazylyl silicate*,  $(\text{C}_6\text{H}_3\text{Me}_2)_4\text{SiO}_4$ , forms a thick colourless oil which is not solidified when cooled with ice and salt; it boils at 453–457°.

*Tetrortho-xylyl silicate* is obtained as a thick colourless oil boiling at 460° under normal pressure, and at 350–360° under 120 mm. pressure; it may be crystallised by cooling.

*Tetrisobutylphenyl silicate*,  $(\text{C}_4\text{H}_9\cdot\text{C}_6\text{H}_4)_4\text{SiO}_4$ , is a thick colourless oil; it boils at 380° under 120 mm. pressure; on cooling with ice and salt, it forms a glass-like mass.

*Tetrisoamylphenyl silicate*,  $(\text{C}_5\text{H}_{11}\cdot\text{C}_6\text{H}_4)_4\text{SiO}_4$ , is a thick colourless

oil; boils at 390—397° under 118 mm. pressure; when cooled with ice and salt, it forms a crystalline mass.

*Tetrathymyl silicate*,  $(C_{10}H_{13})_4SiO_4$ , forms long colourless prisms, melts at 47—48°, and distils at 450° under normal pressure.

*Tetracarvacryl silicate*,  $(C_{10}H_{13})_4SiO_4$ , forms a thick colourless oil which after a time becomes dichroic; it does not solidify when cooled with ice and salt; it boils between 380—390° under 118 mm. pressure.

*Tetramenthyl silicate*,  $(C_{10}H_{19})_4SiO_4$ , crystallises from dry benzene in colourless prisms, melts at 82°, and boils at 350° under 155 mm. pressure.

*Tetra- $\alpha$ -naphthyl silicate*,  $(C_{10}H_7)_4SiO_4$ , boils between 425—430° under 130 mm. pressure; the  $\beta$ -compound was also prepared; it boils at 430° under 133 mm. pressure.

A. P.

**Action of Sodium Mercaptide on Phenyl Salts.** By R. SEIFERT (*J. pr. Chem.* [2], 31, 462—480).—Thiophenol and phenol stand in the same relation to one another as regards their acid properties as do mercaptan and alcohol. That phenol is a stronger acid than mercaptan is shown by the reaction which takes place when sodium mercaptide is mixed with any phenyl salt.

By heating equal molecules of *diphenyl carbonate* and sodium ethoxide, sodium salicylate is obtained; if the ethoxide be replaced by mercaptide, only half the diphenyl carbonate is attacked, and some high-boiling sulphuretted products are obtained. By using twice the quantity of sodium mercaptide, the reaction goes quite smoothly, with formation of sodium phenoxide and ethyl dithiocarbonate. The two substances are rubbed together, and the products separated by water.

*Phenyl formate*, prepared according to Nencki's method by heating formic acid and phenol with phosphorus oxychloride, is attacked by sodium mercaptide in probably the same way as the carbonate, but the ethyl thioformate is at once decomposed by the weak alkaline solution.

*Phenyl acetate* yields ethyl thioacetate with sodium mercaptide; the two bodies should be mixed together with addition of ether.

*Diphenyl succinate* treated in the same way as the acetate yields sodium phenate and ethyl dithiosuccinate as a colourless oil smelling of garlic and boiling with decomposition at 270—271°.

*Triphenyl citrate*, prepared by heating phenol and dry sodium citrate with phosphorus oxychloride, forms colourless needles which melt at 124.5°, are insoluble in water, and easily soluble in alcohol. Treated with sodium mercaptide and ether, it yields ethyl trithiocitrate as a yellowish oil smelling like mercaptan, and decomposing completely on distillation.

*Phenyl benzoate* and sodium mercaptide yield sodium phenoxide and ethyl thiobenzoate.

*Phenyl salicylate*, prepared by Nencki's reaction, crystallises from methyl alcohol in colourless rhombic plates which melt at 42—42.5°, are inodorous, insoluble in water and soluble in alcohol; its alcoholic solution smells like oil of wintergreen. Boiling caustic soda solution

saponifies it, whilst with the cold concentrated solution it forms sodium phenyl salicylate; the same substance is also formed when phenyl salicylate is treated with sodium mercaptide, and the reaction was therefore tried with a salicylate in which the phenol hydrogen atom was replaced by an alcohol radical.

*Phenyl methylsalicylate* prepared like the salicylate forms white six-sided prisms of melting point  $59^{\circ}$ ; treated with sodium mercaptide, it yields *ethyl thiomethylsalicylate* as a colourless oil which boils at  $197\text{--}198^{\circ}$  at 80 mm. pressure.

The above reactions show that alcohol, mercaptan, phenol, and thiophenol form a series in which the basic properties decrease, and the acid properties increase, from left to right. This consideration led to the study of the reaction taking place when diphenyl carbonate is acted on by two molecules of sodium ethoxide: the expected result took place, diethyl carbonate and sodium phenate being formed.

In the preparation of phenyl salicylate, it was observed that on distillation it was completely decomposed with evolution of carbonic anhydride into phenol and a syrupy substance which on purification crystallised from alcohol in long silky needles of melting point  $170^{\circ}$ , and which proved to be orthobenzophenone oxide. J. K. C.

**Carvoxime-derivatives.** By H. GOLDSCHMIDT and R. ZÜRRER (*Ber.*, **18**, 1729—1733).—Carvoxime (Abstr., 1884, 1138) crystallises from alcohol in large colourless transparent plates; it melts at  $71^{\circ}$ , and partially distils at  $240^{\circ}$ , the greater part, however, is decomposed.

*Methylcarvoxime*,  $C_{10}H_{14}NOMe$ , is formed by heating an alcoholic solution of carvoxime with sodium ethoxide and methyl iodide; it is a colourless liquid, smelling like carrots; it is decomposed by distillation.

*Benzoylcarvoxime*,  $C_{10}H_{14}NO\bar{B}z$ , is obtained by treating an ethereal solution of carvoxime with benzoic chloride; the crystalline mass obtained is purified by recrystallisation from light petroleum, and is obtained in tufts of white sparkling needles; it melts at  $95^{\circ}$ , and is soluble in alcohol and benzene.

*Carvoxime hydrochloride*,  $C_{10}H_{14}NOH.HCl$ , is obtained as a white crystalline mass on passing hydrogen chloride through an ethereal solution of carvoxime; on the addition of water or by heating to  $100^{\circ}$ , it is decomposed into hydrochloric acid and carvoxime.

*Hydrochlorocarvoxime*,  $C_{10}H_{16}ClNO$ , a compound isomeric with the above, is obtained when hydrogen chloride is passed through a solution of carvoxime in methyl alcohol. On pouring the clear saturated solution into water, a voluminous crystalline precipitate is obtained; this may be purified by recrystallisation from light petroleum, when it is obtained in thick lustrous white prisms and tablets. It melts at  $132.5^{\circ}$ , and is soluble in the usual solvents; it may be heated to  $162.5^{\circ}$  without decomposition.

When carvoxime is heated for a short time with dilute sulphuric acid at  $100^{\circ}$ , carvol is formed.

The percentage composition, melting point, and general properties

of carvoxime are identical with those of nitrosohesperidene described by Tilden and Shenstone (this Journal, 1877, i, 559). If, therefore, the constitution of carvol (Abstr., 1884, 1138) be correct, carvene should have the formula  $\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CPr}$ . As, however, this formula does not contain an asymmetric carbon-atom, it hardly agrees with the optical activity of carvene. A. P.

**New Mode of Formation of Catechol.** By J. MEUNIER (*Compt. rend.*, **100**, 1591—1593).—When benzene hexachloride is heated with 100 times its weight of water at 190—200° for 10 hours in sealed tubes from which the air has been expelled, the products include a considerable proportion of catechol melting at 104°. No pyrogallol is formed. If crude benzene hexachloride is used, the benzene tetrachloride which it contains is also found amongst the products, but it pre-existed in the crude substance, and is not formed by the action of water on the pure hexachloride. C. H. B.

**Action of Pyrogallol on Copper and Iron Salts.** By P. CAZENEUVE and G. LIROSSIER (*Compt. rend.*, **101**, 56—59).—When solutions of pyrogallol and ferrous sulphate are mixed in complete absence of oxygen, no change is apparent, but the introduction of a small quantity of oxygen brings about the formation of the well-known blue coloration. If, however, the pyrogallol solution is not fresh, but has been slightly oxidised, the blue coloration is produced at once. The oxygen combines simply with the pyrogallol, and does not oxidise the ferrous sulphate, since ferric salts cannot exist in presence of pyrogallol, but are instantly reduced. A mixture of a ferric salt with excess of pyrogallol gives no coloration with thiocyanates, and no precipitate with ammonium succinate.

When solutions of pyrogallol and ferric chloride are mixed out of contact with oxygen, a fugitive blue coloration is also produced, but almost instantly changes to a deep reddish-brown coloration. Addition of an alkali causes the reappearance of the blue colour, and if added in excess changes it to violet. In this reaction, the ferric chloride is reduced, and the ferrous salt combines with the pyrogallol, but the blue compound is at once decomposed by the hydrochloric acid which has been liberated in the process of reduction. The dark brown colour is simply due to oxidised pyrogallol. The addition of alkali neutralises the free acid, and thus renders the formation of the blue compound possible. All strong acids prevent the formation of this compound, but feebler acids, such as boric and acetic, have not the same effect. The blue coloration is due to the combination of partially oxidised pyrogallol with a ferrous salt. If a current of air is blown through the blue liquid, or if pyrogallol is mixed with a large excess of ferric chloride and an alkali then added, a black precipitate is formed by the oxidation of the blue compound.

Pyrogallol does not give any coloration with ammoniacal cuprous chloride out of contact with oxygen, but the introduction of a trace of this gas causes the formation of a deep brownish-black compound. Cupric sulphate is immediately reduced by pyrogallol, and on addition

of an alkali a black coloration is produced which is changed to red by excess of ammonia, and is destroyed by hydrochloric acid. Cupric acetate gives an immediate black coloration without addition of an alkali. It is evident, therefore, that the action of pyrogallol on copper salts is strictly analogous to its action on iron salts.

C. H. B.

**Oxidation of Phenol by Nitrobenzene.** By M. SIEGFRIED (*J. pr. Chem.* [2], **31**, 542—543).—If a solution of phenol in excess of 24 per cent. aqueous soda be shaken in the cold with nitrobenzene, the liquid assumes a brick-red colour, which on slight warming turns black. After heating at 150° for some hours, sodium oxalate separates out, whilst azobenzene and a black resin remain in the mother-liquor together with sodium carbonate.

J. K. C.

**Chlorinated and Brominated Hydrocarbons from Aromatic Amines.** By K. GASIOROWSKI and A. F. WÄYSS (*Ber.*, **18**, 1936—1942).—The authors recently showed that diazobenzene chloride or bromide yields considerable quantities of chloro- and bromo-benzene when heated with the corresponding hydracids (this vol., p. 525); similar observations had been made earlier by Hübner and Majert (this Journal, 1873, 1135); by Jackson (*Proc. Amer. Acad.*, 1876); and by Liebermann (this Journal, 1877, 597).

From the results of his investigation, the author draws the following conclusions. If aromatic amine hydrochlorides are converted into the corresponding diazo-compounds, and then heated with excess of concentrated hydrochloric acid, there are formed, not phenols only, as occurs if the acid is not in excess, but also the corresponding chlorinated hydrocarbons. The same holds good for the hydrobromides when treated with hydrobromic acid.

The following statement shows the yield calculated on the weight of the amine employed:—Chlorobenzene 53 per cent., bromobenzene 60 per cent., orthochlorotoluene 52 per cent., parachlorotoluene 60 per cent.,  $\alpha$ -chloronaphthalene 45 per cent.,  $\beta$ -chloronaphthalene 50 per cent.,  $\beta$ -bromonaphthalene 37 per cent. The amount of the phenols formed was about half that of the chloro- or bromo-derivatives.

A. J. G.

**Cyananiline and some of its Derivatives.** By A. SENF (*J. pr. Chem.* [2], **31**, 543—544).—By the action of nitrous acid on cyananiline dissolved in glacial acetic acid, a crystalline compound of the formula  $C_{14}H_{15}N_3O_6$  is obtained, which, when heated alone or with water, yields phenyl isocyanide. Heated for some time with nitrous acid, cyananiline yields a substance which is converted into paranitraniline by treatment with caustic soda. The author is engaged in investigating these and other cyanogen-derivatives of aniline.

J. K. C.

**Benzoyl-derivatives of Phenylhydrazine.** By J. TAFEL (*Ber.*, **18**, 1739—1744).—This research was undertaken to determine the formulæ of the mono- and di-benzoylphenylhydrazines obtained by E. Fischer (*Abstr.*, 1878, 308).

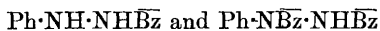
*Methyldibenzoylphenylhydrazine*,  $Ph \cdot N\bar{B}z \cdot N\bar{B}z \cdot Me$ , was obtained by heating sodiumdibenzoylphenylhydrazine with methyl iodide. It

forms soft, white, glistening crystals which melt at  $145^{\circ}$ , are insoluble in water and light petroleum, but dissolve readily in acetone, chloroform, and carbon bisulphide, and in boiling ethyl and methyl alcohols and benzene. When quickly distilled with dry potash, it yields benzoic acid, aniline, methylamine, and *methylphenylhydrazine*,  $\text{Ph}\cdot\text{NH}\cdot\text{NHMe}$ . This latter base is an unstable colourless oil, which becomes rapidly coloured when exposed to the air, whilst the odour of azomethylphenyl becomes perceptible. Its *sulphate* melts at  $180^{\circ}$ , is sparingly soluble in alcohol, easily in water, and reduces Fehling's solution in the cold; the oxalate crystallises in needles; the chloride in scales. A similar decomposition is produced if the alkali is replaced by strong hydrochloric acid, but the yield of hydrazine is much smaller.

*Azomethylphenyl*,  $\text{Ph}\cdot\text{N}_2\cdot\text{Me}$ , is formed by the oxidation of the hydrazine, mercuric oxide proving the best oxidising agent. It is a yellowish highly volatile oil, which distils, but with much decomposition, at  $150^{\circ}$ ; it is easily volatile in steam, and has a strong penetrating odour. It resembles Fischer's azoethylphenyl in properties, but yields only very little of the hydrazine when reduced with sodium amalgam.

*Methylmonobenzoylphenylhydrazine*,  $\text{Ph}\cdot\text{NMe}\cdot\text{NH}\bar{\text{Bz}}$ , was obtained by heating sodium monobenzoylphenylhydrazine with methyl iodide. It forms white needles melting at  $153^{\circ}$ ; it is very sparingly soluble in water and alkalis, easily so in boiling alcohol, chloroform, benzene, hydrochloric acid, and glacial acetic acid. A hydrochloric acid solution is turned red by a trace of nitrous acid, dark brown by a larger quantity. When digested with concentrated hydrochloric acid at  $100^{\circ}$ , the hydrazine is decomposed into benzoic acid, and the unsymmetrical *methylphenylhydrazine*,  $\text{Ph}\cdot\text{NMe}\cdot\text{NH}_2$ .

The decomposition products formed from the methylbenzoyl-derivatives by alkalis and acids, prove the correctness of the formulæ ascribed to them, and consequently establishes the formulæ



for the mono- and di-benzoylphenylhydrazines respectively.

L. T. T.

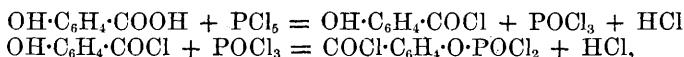
**Paramonochloracetophenone.** By H. GAUTIER (*Bull. Soc. Chim.*, **43**, 602—606).—Paramonochloracetophenone,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{COMe}$ , is obtained by acting on monochlorobenzene with acetic chloride at a low temperature in the presence of aluminium chloride; it is solid at ordinary temperatures, melts at  $20^{\circ}$ , forming a very refractive colourless liquid, sp. gr. 1.19 at  $20^{\circ}$ ; it is almost insoluble in water, but miscible in all proportions with ether or alcohol; its odour is pungent, but somewhat similar to that of acetophenone; it boils at  $230$ — $231^{\circ}$ , its vapour-density being 5.345; on oxidation with alkaline permanganate, it yields parachlorobenzoic acid; it does not unite with hydrogen sodium sulphate. Phosphorus pentachloride acts on it vigorously, but the products of this reaction have not been examined.

A. P.

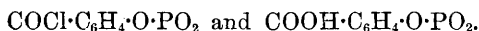
**Action of Phosphoric Chloride on Salicylic Acid.** By R. ANSCHÜTZ (*Annalen*, **228**, 308—321).—The action of phosphoric chloride on winter-green oil and on salicylic acid has been investigated

by Chiozza (*Annalen*, **83**, 317), Gerhardt (*ibid.*, **89**, 363), Drion (*ibid.*, **92**, 314), Couper (*ibid.*, **109**, 369), Kolbe and Lautemann (*ibid.*, **115**, 183), Kekulé (*ibid.*, **117**, 146), and Schreib (*Abstr.*, 1880, 557).

The author obtains the *orthochlorocarbonylphenylorthophosphoric dichloride*,  $C_6H_4(COCl)(O \cdot POCl_2)$  [1 : 2] by the reaction of equivalent quantities of phosphorus pentachloride and dry salicylic acid. On distilling the product under a pressure of 11 mm., the pure substance passes over at a temperature of  $168^\circ$ . It is identical with Couper's "*trichlorophosphate de salicyle*." The reaction really takes place in two stages—



The chloride is a colourless highly refractive liquid, sp. gr. 1.55413 at  $20^\circ$  compared with water at  $4^\circ$ . It is partially decomposed when distilled under the ordinary atmospheric pressure, yielding the *monochloride*  $C_7H_4ClPO_4$ . This substance can be easily obtained by the action of anhydrous oxalic acid on the dichloride. It melts at  $80^\circ$ , and boils at  $181^\circ$  under a pressure of 11 mm. On exposure to moist air, it loses hydrogen chloride, and changes into a deliquescent crystalline compound which melts at  $145^\circ$ . The author suggests the following formulæ for the monochloride and its derivative :—



W. C. W.

**$\beta$ -Sulphophthalic Acid from Phthalic Acid.** By A. RÉE (*Ber.*, **18**, 1629—1631; compare Graebe, this vol., p. 902).—Loew (*Annalen*, **143**, 259) prepared this substance by heating phthalic acid with an excess of sulphuric anhydride at  $100$ — $105^\circ$ , but the yield at this temperature is very small. A complete sulphonation may be effected by heating phthalic anhydride (20 grams) with sulphuric acid containing 65 per cent. anhydride for 10 hours at  $170$ — $180^\circ$ . In order to effect the sulphonation at atmospheric pressure, the phthalic anhydride is dissolved in sulphuric acid (containing 25 per cent. anhydride), the solution heated at  $190$ — $200^\circ$ , and a slow current of sulphuric anhydride passed into it until the addition of water to a sample of the product no longer produces turbidity. The  $\beta$ -sulphophthalic acid is best isolated by means of the acid barium salt,  $(C_8H_5O_4 \cdot SO_3)_2Ba \cdot 5H_2O$ . On fusing the acid with sodium hydroxide,  $\beta$ -hydroxyphthalic acid (this Journal, 1877, ii, 784) is obtained. The acid liberated from the mother-liquor of the barium salt yielded traces of salicylic acid when fused with soda, from which it appears that in the above reaction a small quantity of  $\alpha$ -sulphophthalic acid is also formed.

A. K. M.

**Dinitro- and Diamido-amarine.** By A. CLAUS and C. WITT (*Ber.*, **18**, 1670—1677).—Amarine was treated under various conditions with nitric acid of different strengths, in the hope of obtaining the two compounds melting at  $142^\circ$  and  $95^\circ$  respectively, mentioned in a previous paper (*Abstr.*, 1883, 203). A complicated mix-

ture of yellow and red products was formed, however, which were very difficult to isolate. Under certain conditions, two colourless substances, *amarine nitrate* and *dinitramarine nitrate* are produced. In order to obtain amarine nitrate, finely powdered amarine (1 part) is heated with nitric acid (8 parts) of sp. gr. 1.3 at 65–68° until the amarine melts and forms a limpid layer floating on the nitric acid. On adding the cooled product to iced water, amarine nitrate,

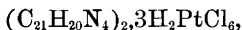


separates, and when recrystallised from alcohol, glacial acetic acid, or acetone, forms large vitreous, colourless crystals, sparingly soluble in water, insoluble in ether, and which melt at 165° (uncorr.).

*Dinitramarine nitrate*,  $\text{C}_{21}\text{H}_{16}\text{N}_2(\text{NO}_2)_2, \text{HNO}_3$ , is prepared by heating amarine nitrate with 10 times its weight of fuming nitric acid at 55–60° for 15–20 minutes. The product is added when cold to iced water, and the precipitate produced is extracted with alcohol until the residue of dinitramarine nitrate becomes perfectly white. It crystallises from glacial acetic acid in small colourless prisms or needles melting at 170° (uncorr.). *Dinitramarine* may be separated from the nitrate by the action of ammonia, as a white granular powder, which, however, cannot be dried without partial oxidation. The *hydrochloride*,  $\text{C}_{21}\text{H}_{16}\text{N}_2(\text{NO}_2)_2, \text{HCl}$ , and *platinochloride*,  $(\text{C}_{21}\text{H}_{16}\text{N}_4\text{O}_4)_2, \text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$ , are described.

On oxidising dinitramarine nitrate with chromic acid, benzoic and paranitrobenzoic acids are produced, the latter in the larger amount, and the same products are obtained by oxidation with nitric acid. The two nitro-groups must therefore be united to two different benzene nuclei, and in the para-position to the side-chain.

*Diamidoamarine*,  $\text{C}_{21}\text{H}_{16}\text{N}_2(\text{NH}_2)_2$ , is insoluble in water, readily soluble in ether and alcohol. It begins to decompose at about 210° without melting. Its salts exist in solution only in presence of an excess of acid, from which solutions they may be crystallised. The *hydrochloride*,  $\text{C}_{21}\text{H}_{16}\text{N}_2(\text{NH}_2)_2, 3\text{HCl}$ , and *platinochloride*,



are described.

When finely powdered amarine is treated with well-cooled fuming nitric acid in a vessel surrounded by ice, and the brown solution obtained poured into iced water, *mononitramarine nitrate*,



separates. It crystallises in slender white needles, is sparingly soluble in cold alcohol, softens at about 130°, and decomposes at 134° without melting. The free mononitramarine, which has not yet been obtained in a crystalline state, separates on treating the solution of the nitrate in alcoholic ammonia with water. A. K. M.

**An Allotropic Modification of Amarine.** By A. CLAUS (*Ber.*, 18, 1678–1679).—When amarine melting at 100° is boiled with water, it gradually loses its property of melting under boiling water, and becomes converted into a granular mass, which, according to cir-



cumstances melts at 107°, 110°, 113°, 120°, and even at 126° (uncorr.), if it is frequently and vigorously boiled. On crystallising the product from ether, it is obtained in prisms melting at 100°, and the melting point may again be raised to 126° by boiling with water. The high melting modification may be heated at 110° without undergoing change. In its behaviour to solvents, it does not show any marked difference from the lower melting variety. The composition of the amarine melting at 126° agrees with the formula  $C_{21}H_{18}N_2$ .

The above may account for the different melting points which have been assigned to amarine. A. K. M.

**Decomposition of Aromatic Fumarates by Heat.** By R. ANSCHÜTZ and Q. WIRTZ (*Ber.*, 18, 1947—1949).—Perkin has stated (*Trans.*, 1881, 562) that fumaric chloride is formed by distilling maleic anhydride with phosphoric chloride. By mixing these substances and distilling under reduced pressure (11 mm.) as soon as the reaction was completed, the authors obtained maleic chloride; when, however, the mixture was allowed to remain three months before distillation, fumaric chloride appeared to be formed.

*Phenyl fumarate* crystallises in white needles, and melts at 161—162°. When quickly distilled, it passes over in part unaltered, whilst the remainder is converted into carbonic anhydride and stilbene; if the distillation is conducted slowly, the conversion into stilbene is complete. If the reaction is stopped when half the theoretical amount of carbonic anhydride has been evolved, and the residue distilled under reduced pressure, phenyl cinnamate is obtained, together with much stilbene.

*Paracresyl fumarate* is sparingly soluble in alcohol, and melts at 162°. When heated, it loses carbonic anhydride, and is converted into a mixture of two substances, which can be separated by their different solubilities in alcohol. The more sparingly soluble substance, *dimethylstilbene*,  $C_6H_4Me \cdot CH : CH \cdot C_6H_4Me$ , melts at 179°, and yields a bromide melting at 203—204° with decomposition. The other substance melts at 79°, crystallises in silvery plates, is readily soluble in alcohol, and probably is cresyl methylcinnamate. A. J. G.

**New Method of Preparing Aromatic Hydrocarbons.** By R. ANSCHÜTZ (*Ber.*, 18, 1945—1946).—Phenyl fumarate when distilled yields stilbene; as it seemed most probable in this reaction that the phenyl fumarate is first converted into phenyl cinnamate, and that this by further loss of carbonic anhydride yields stilbene, several cinnamates were prepared and their products of decomposition by heat investigated.

*Phenyl cinnamate* melts at 72·5°, is readily soluble in alcohol, boils without decomposition at 205—207° under 15 mm. pressure, but when slowly distilled at the ordinary pressure is resolved into stilbene and carbonic anhydride according to the equation  $CHPh : CH \cdot COOPh = CO_2 + CHPh : CHPh$ .

*Paracresyl cinnamate*,  $CHPh : CH \cdot COO \cdot C_6H_4Me$ , is sparingly soluble in alcohol, melts at 100—101°, and boils without decomposition at 230° under 15 mm. pressure. When distilled at the ordinary pres-

sure, it yields *methylstilbene*,  $\text{CHPh} : \text{CH} \cdot \text{C}_6\text{H}_4\text{Me}$  [ $\text{CH} : \text{Me} = 1 : 4$ ]. This crystallises in plates having a blue fluorescence, melts at  $120^\circ$ , and when treated in chloroform solution with bromine yields a bromide melting at  $186$ – $187^\circ$ , and very sparingly soluble in boiling alcohol.

*Thymyl cinnamate*,  $\text{CHPh} : \text{CH} \cdot \text{COOC}_6\text{H}_3\text{MePr}$ , melts at  $69$ – $70^\circ$ , and boils at  $239$ – $240^\circ$  under 15 mm. pressure. When heated at the ordinary pressure, it yields carbonic anhydride and liquid products not yet investigated.

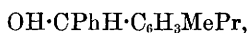
$\beta$ -*Naphthyl cinnamate*,  $\text{CHPh} : \text{CH} \cdot \text{COO} \cdot \text{C}_{10}\text{H}_7\beta$ , melts at  $101$ – $102^\circ$ , and when heated at the ordinary pressure yields a hydrocarbon sparingly soluble in alcohol. This forms silvery plates, melts at  $145^\circ$ , and is readily soluble in chloroform; the bromide melts at  $192^\circ$ , is readily soluble in chloroform, very sparingly in boiling alcohol.

Phenyl succinate is completely decomposed with evolution of carbonic anhydride when slowly heated. The products are under investigation.

A. J. G.

**Alkylated Diphenylketones, and their Conversion into Alkylated Anthracenes.** By A. CLAUS and K. ELBS (*Ber.*, 18, 1797–1799).—Elbs and Larsen (this vol., p. 261) found that paraxylyl phenyl ketone is converted by boiling into methylanthracene. The authors have examined other ketones of this class. Larsen has found that metaxylene, when treated with benzoic chloride and aluminium chloride, forms two isomeric ketones, both of which lose water and form methylanthracene.

*Paracymyl phenyl ketone*,  $\text{Ph} \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}_3\text{H}_7$ , has been obtained by Hartmann as a thick viscid pale yellow oil, which boils at  $223$ – $224^\circ$  (uncorr.), under 35 mm. pressure, and remains liquid below  $0^\circ$ . When reduced, it yields *paracymyl phenyl carbinol*,



a thick, almost colourless oil boiling at  $327^\circ$  (uncorr.). When heated for some days at its boiling point, the ketone was converted into a dark brown tarry mass, from which the authors isolated a small quantity of anthracene, but no trace of a propylated anthracene was obtained. The formation of anthracene was probably due to the presence of orthotoluphenone formed by retrogressive de-propylation of the cymene during the reaction with aluminium chloride.

Markstahler has similarly examined the ketone obtained by Louise (*Abstr.*, 1883, 577) from mesitylene, and also that from pseudocumene, and finds that in these cases neither heating nor the action of dehydrating agents causes the formation of anthracene-derivatives.

It is thus clear that this elimination of water to form anthracene-derivatives is not a property common to all alkylated diphenyl ketones; further investigation is needed to determine under what conditions it does occur.

L. T. T.

**Chlorinated Quinones and Quinols.** By M. NIEMEYER (*Annalen*, 228, 322–339).—Hebebrand (*Abstr.*, 1883, 60) has pointed out that benzoquinone unites with ortho- and para-, but not

with meta-nitraniline to form crystalline compounds. The author finds the chlorinated quinones on the other hand combine with meta- but not with ortho- or para-nitraniline.

The compounds of metanitriline with chlorinated quinones are deposited on mixing solutions of their components in hot benzene. They are decomposed by water, alcohol, and acetic acid, but may generally be recrystallised from benzene without decomposition. *Monochloroquinonemetanitriline* forms dark-green crystals which readily effloresce;  $\alpha$ -*dichloroquinonemetanitriline*,



forms compact crystals melting at  $110^\circ$ ;  $\beta$ -*dichloroquinone* only unites with 1 mol. of metanitriline to form the compound



which crystallises in dark prisms, possessing a green metallic lustre. It melts at  $112^\circ$ .

*Trichloroquinonemetanitriline*,  $\text{C}_6\text{HCl}_3\text{O}_2, 2(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2)$ , forms dark-green prisms with a metallic lustre melting at  $108^\circ$ , and *tetrachloroquinonemetanitriline*,  $\text{C}_6\text{Cl}_4\text{O}_2, 2(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2)$ , black crystals.

Crystalline compounds of aniline and the chlorinated quinols are formed when aniline is added to a solution of a chlorinated quinol in hot water or benzene. Most of these bodies may be recrystallised from benzene. *Monochloroquinol* unites with 2 mols. aniline and with 2 mols. paratoluidine to form compounds crystallising in glistening plates, which melt at  $92^\circ$  and  $90^\circ$  respectively. The compound  $\text{C}_6\text{H}_2\text{Cl}_2(\text{OH})_2, 2\text{NH}_2\text{Ph}$  forms thick tables or plates which melt at  $112^\circ$ . The corresponding  $\beta$ -compound could not be obtained in the solid state.  $\alpha$ -*Dichloroquinoldiparatoluidine* is deposited from water in plates and from benzene in needles, which melt at  $114^\circ$ . The corresponding  $\beta$ -compound melts at  $72^\circ$ .

*Trichloroquinolmonaniline*,  $\text{C}_6\text{HCl}_3(\text{OH})_2, \text{NH}_2\text{Ph}$ , forms needles melting at  $60^\circ$ ; the *dianiline*,  $\text{C}_6\text{HCl}_3(\text{OH})_2, (\text{NH}_2\text{Ph})_2$ , is formed in benzene, but not in aqueous solutions; it crystallises in rhombic plates, which melt at  $67^\circ$ . *Tetrachloroquinolmonaniline* melts at  $115^\circ$ ; it is not very stable, and is decomposed by recrystallisation from benzene.

*Aniline-derivatives of Chlorinated Quinones*.—*Monochloroquinone* and *quinone* yield the same dianilidoquinone.  $\alpha$ -*Dichloroquinone* forms a mono- and a dianilido-derivative. The former crystallises in beautiful blue plates melting at  $180^\circ$ ; it dissolves freely in alcohol, ether, and chloroform. The dianilide is identical with chloranil-anilide from chloranil. The *monanilide* of  $\beta$ -*dichloroquinone* crystallises in bluish-violet needles or plates melting at  $154^\circ$ , and the *dianilide* in brown plates which melt at  $262^\circ$ . The author, like Andresen (Abstr., 1884, 431), was unable to prepare monochloroquinonedianilide from trichloroquinone, as described by Knapp and Schulz (*ibid.*, 1882, 511).

*Dianilidodichloroquinone*,  $\text{C}_6\text{Cl}_2(\text{NHPh})_2\text{O}_2$ , is formed when aniline is added to an alcoholic solution of trichloroquinone; its properties have been described by Andresen (*loc. cit.*). *Monanilido-*

*trichloroquinone*,  $\text{NHPh} \cdot \text{C}_6\text{Cl}_3\text{O}_2$ , crystallises in blue plates, freely soluble in alcohol, benzene, and chloroform. On warming the alcoholic solution with aniline, dianilidodichloroquinone is produced. The sole product of the action of aniline on tetrachloroquinone is the well-known chloranilanilide.

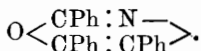
Ortho- and para-toluidine resemble aniline in their action on chlorinated quinones. The nitranilines readily enter into reaction with the chloroquinones, forming sparingly soluble nitranilides.

W. C. W.

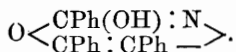
**Benzoïn-anilide and its Derivatives.** By K. VOIGT (*J. pr. Chem.* [2], 31, 544).—Contrary to Schiff's statement, the author has obtained benzoïn-anilide by the action of aniline on benzoïn, and is engaged in investigating its nitroso- and other derivatives.

J. K. C.

**Benzil-derivatives.** By M. HENIUS (*Annalen*, 228, 339—355).—By the action of ammonia on benzil, Laurent obtained (*Gerhardt Lehrb. org. Chem.*, 3, 309) three derivatives: *imabenzil*, *benzilimide*, and *benzilam*. Imabenzil,  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_4$ , is best prepared by pouring a hot concentrated alcoholic solution of benzil into excess of ammonia. It decomposes at  $140^\circ$  yielding benzaldehyde, benzilimide, and benzilam. It is also decomposed by prolonged boiling with alcohol, acetic acid, or acetic anhydride; in the latter case, it is converted into benzil. The products of the action of alcoholic potash on imabenzil are benzilimide, benzilam, and benzil, or benzil and benzoic acid, according to the strength of the reagent and the duration of the reaction. Strong sulphuric acid dissolves imabenzil, with formation of benzaldehyde. If the solution is immediately poured into water, benzilam is precipitated; but if it is left at rest for some time before dilution, benzil will be produced. Two nitro-products are obtained by the action of strong nitric acid on benzil. One of these compounds is sparingly soluble in alcohol and ether, and melts between  $275^\circ$  and  $280^\circ$ . It is also formed by the nitration of benzilam, and is perhaps a dinitro-benzilam. Japp (*Trans.*, 1882, 12) has shown that the composition of *benzilimide* is represented by the formula  $\text{C}_{21}\text{H}_{17}\text{NO}_2$ , and that the constitution of *benzilam* may be regarded as



Now, as benzilimide is easily converted into benzilam by dehydrating agents, the constitutional formula for benzilimide will be



Benzilam is easily obtained by the action of strong sulphuric acid on imabenzil. On nitration, it yields the same products as imabenzil. The mononitro-derivative crystallises in needles melting at  $178$ — $182^\circ$ . It is converted into the dinitro-compound by strong nitric acid.

W. C. W.

**Amido- and Hydroxy-phenanthraquinones.** By R. ANSCHÜTZ and P. MEYER (*Ber.*, 18, 1942—1944; compare *Abstr.*, 1880, 891, and 1884, 328, 754).—When a nitroanthraquinone is boiled with tin and

hydrochloric acid, the nitro-groups are first attacked, the amido-hydrochloride separating as a yellowish-red, sparingly soluble powder; by continued heating, this is converted into the white, sparingly soluble amidoquinol hydrochloride, which is readily reoxidised by ferric chloride. Water decomposes the amido-hydrochlorides into hydrochloric acid and the free bases. Nitrous acid converts them into diazo-compounds, from which, on boiling with water, the corresponding hydroxy-compounds are obtained.

*Paramidophenanthraquinone*,  $C_{14}H_7O_2 \cdot NH_2$ , crystallises in violet-black needles, melts at  $200^\circ$  with decomposition, is readily soluble in alcohol, sparingly in hot water, the solution having a red-violet colour. The hydrochloride crystallises in feathery groups of yellowish-red needles.

*Paramidophenanthraquinol hydrochloride* crystallises in white needles.

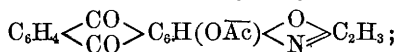
*Parahydroxyphenanthraquinone*,  $C_{14}H_7O_2 \cdot OH$ , forms slender brownish-red needles, can be sublimed by careful heating, and dissolves in aqueous soda with yellowish-green colour. It is not identical with the hydroxy-derivative previously prepared. The *acetyl*-derivative crystallises in reddish-yellow needles, and melts with decomposition at  $200-210^\circ$ .

*Paradiamidophenanthraquinone*,  $C_{14}H_5O_2(NH_2)_2$ , crystallises in violet-black needles, and does not melt at  $310^\circ$ . The hydrochloride forms yellow crystalline plates. *Paradiamidophenanthraquinol hydrochloride* crystallises in white needles.

*Paradihydroxyphenanthraquinone*,  $C_{14}H_5O_2(OH)_2$ , forms microscopic, translucent, blackish-brown needles. The diacetyl-derivative crystallises in yellowish-red needles.

A. J. G.

**Constitution and Derivatives of  $\beta$ -Amidoalizarin.** By H. ROEMER (*Ber.*, 18, 1666—1670).—The preparation and properties of amidoalizarin were described by Roemer and Schunk (*Abstr.*, 1879, 654). When it is heated with acetic anhydride at  $180^\circ$ , a brown crystalline product is formed, which is insoluble in potash, but which is gradually rendered soluble by crystallisation from alcohol or acetic acid, the melting point of the substance being raised simultaneously. The solution in potash is blue, but is distinguished from that of the amidoalizarin by the stability of the colour, and by two strong absorption-bands in its spectrum. The compound may be crystallised from benzene or acetic anhydride, and forms lustrous, yellowish-brown crystals melting at  $238-240^\circ$ ; it sublimes in bright yellow scales. Its composition agrees with that of a diacetyl-derivative of amidoalizarin, minus the elements of a molecule of water, and its properties likewise indicate it to be *ethenylacetylamilidoalizarin*,



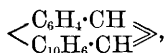
and since the formation of such an ethenyl-group can only take place when the amido- and hydroxyl-groups are in the ortho-position relatively one to the other, the above formula proves amidoalizarin to have the constitution  $C_6H_4 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C_6H(OH)_2 \cdot NH_2$ .

When ethenylacetylamilidoalizarin is boiled with strong hydrochloric acid, a yellow solution is obtained which deposits the hydrochloride of  $\beta$ -amidoalizarin on cooling; the crystals become red when washed with water, and possess the properties assigned by Schunk and Roemer to  $\beta$ -amidoalizarin. On warming ethenylacetylamilidoalizarin with dilute potash, a yellow solution is first formed which changes to red, purple, violet, and becomes finally blue; hydrochloric acid precipitates a red substance, which is intermediate between ethenylacetylamilidoalizarin and amidoalizarin. It is best prepared by boiling ethenylacetylamilidoalizarin with a mixture of equal parts of glacial acetic acid and water. As the solution cools, lustrous reddish-brown crystals separate, which are completely soluble in potash with blue colour, and melt at  $268-271^\circ$  with evolution of gas. This substance is soluble in alcohol with yellow colour, the solution giving a violet precipitate with alcoholic lead acetate, whilst amidoalizarin yields a red precipitate. Alcoholic copper acetate gives a red solution with the substance, and a green solution with amidoalizarin; concentrated sulphuric acid dissolves it with golden-yellow coloration. It is insoluble in cold, and is converted by boiling hydrochloric acid into amidoalizarin hydrochloride; with sodium carbonate, it yields a violet solution which becomes blue on the addition of potash. Alumina mordants are coloured of a deeper hue by it than by alizarin. On sublimation, it yields principally ethenylacetylamilidoalizarin. These properties, combined with the composition of the compound, indicate it to be diacetylamilidoalizarin,  $C_6H_4 \begin{smallmatrix} CO \\ \diagup \diagdown \\ CO \end{smallmatrix} C_6H(OAc)(OH) \cdot NHAc$ .

When a mixture of benzoic chloride and amidoalizarin is boiled as long as hydrochloric acid is evolved, *benzenylbenzamidoalizarin*,  $C_6H_4 \begin{smallmatrix} CO \\ \diagup \diagdown \\ CO \end{smallmatrix} C_6H(OBz) \begin{smallmatrix} O \\ \diagup \diagdown \\ N \end{smallmatrix} C_7H_5$ , is formed, and separates as a crystalline mass on cooling. It melts above  $300^\circ$ , sublimes in yellow needles, and is almost insoluble in all the ordinary solvents; it is not decomposed by water at  $200^\circ$ , nor by boiling hydrochloric acid, although at  $180^\circ$  amidoalizarin hydrochloride is produced. Boiling aqueous potash has no action on it, whilst alcoholic potash yields a blue solution. Dibenzoylamidoalizarin could not be obtained in a pure condition.

A. K. M.

**Chrysene.** By E. E. BAMBERGER and J. KRANZFELD (*Ber.*, 18, 1931—1934).—From their synthesis of chrysene by passing benzylnaphthylmethane through a red-hot tube, Graebe and Bungener (*Abstr.*, 1879, 807) concluded that it had the constitution



thus making it a phenanthracene, in which phenylene was replaced by naphthylene. In accordance with this assumption, a phenylnaphthalene,  $C_{16}H_{12}$ , can be obtained from chrysoquinone. The authors now confirm this view by preparing from chrysoquinone a series of derivatives analogous to those obtained from phenanthraquinone. That the carbonyl groups in chrysoquinone are probably in the ortho-

position relatively to one another, has already been shown by Bamberger (this vol., p. 807).

*Chrysoglycollic acid*,  $C_{15}H_{10}:C(OH) \cdot COOH$ , is obtained by boiling freshly precipitated chrysoquinone with alkalis, and separates in orange-coloured flocks on acidifying the solution. When pure it is colourless, is very unstable, and is readily soluble in alkalis. The silver salt forms a white precipitate.

*Chrysoketone*,  $C_{16}H_{10}:CO$ , is obtained in small quantity by oxidising chrysoglycollic acid with chromic mixture; a better yield is obtained by distilling chrysoquinone with lead oxide. It crystallises in lustrous brick-red needles, melts at  $130^{\circ}$ , scarcely volatilises with steam, and is readily soluble in ordinary solvents.

*Chrysofluorene alcohol*,  $C_{16}H_{10}:CH \cdot OH$ , is prepared by reducing chrysoketone with zinc and hydrochloric acid. It crystallises in white silky needles or plates, melts at  $166-167^{\circ}$ , sublimes with slight decomposition, and is readily soluble in alcohol, ether, chloroform, and benzene, sparingly in light petroleum. It dissolves in sulphuric acid with reddish-violet coloration, whilst if the acid be added to the alcoholic solution a blue liquid is obtained, from which white flocks separate on heating.

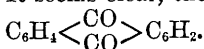
*Chrysofluorene*,  $C_{16}H_{10}:CH_2$ , is obtained by heating chrysoquinone with hydriodic acid and phosphorus at  $150-160^{\circ}$ . It forms silvery white tables, melts at  $187-188^{\circ}$ , and is readily soluble in ether, benzene, and chloroform, more sparingly in cold alcohol. A yellow nitro-derivative, sparingly soluble in alcohol, is formed when its acetic acid solution is treated with nitric acid.

A. J. G.

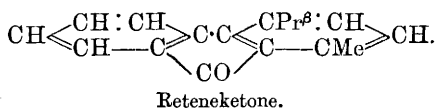
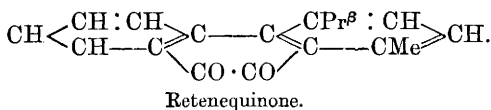
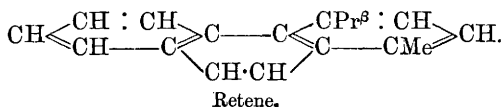
**Constitution of Retene.** By E. BAMBERGER and S. C. HOOKER (Ber., 18, 1750—1755).—In his previous researches (Abstr., 1884, 1040, and this vol., p. 549), Bamberger showed that retenequinone con-

tains the double carbonyl-group, and has the formula  $C_{16}H_{16} \begin{matrix} \diagup CO \\ | \\ \diagdown CO \end{matrix}$ . The present research has for its object the elucidation of the nature of the radicle ( $C_{16}H_{16}$ )".

When treated in alkaline solutions with permanganate, retenequinone yields *hydroxyisopropylidiphenyleneketonecarboxylic acid*,  $C_{17}H_{14}O_4$ , which is a strong acid containing only one carboxyl-group. It may therefore be written  $CO:C_{15}H_{13}O \cdot COOH$ . This, on further oxidation with chromic mixture, yields *diphenyleneketonecarboxylic acid*,  $C_{16}H_8O_3$ . Its silver salt shows it to be bibasic, and the formation of an oxime, indicates the presence of a CO-group. When the silver salt is distilled, diphenyleneketone is produced. The formula must therefore be  $CO:C_{12}H_6(COOH)_2$ , which agrees also with the fact that when fused with potash it yields *diphenyltricarboxylic acid*,  $C_{12}H_7(COOH)_3$ , which gives diphenyl when distilled with lime. The dicarboxylic acid,  $C_{15}H_8O_3$ , when reduced with sodium amalgam, yields fluorene dicarboxylate, from which fluorene was obtained by distilling it with lime. It seems clear, therefore, that retenequinone must contain the nucleus



Of the four remaining carbon-atoms, two must be directly united with the diphenylene nucleus, otherwise a diphenyleneketonecarboxylic acid could not be formed. They may either form another ring or be in the form of two alkyl-groups. The highly hydrogenised state of these four carbon-atoms, and the fact of the first oxidation producing a monobasic acid,  $C_{17}H_{14}O_4$ , point to the alkyl- rather than the ring-constitution. The first carbon-atom lost in the oxidation of  $C_{18}H_{16}O_2$  to  $C_{17}H_{14}O_4$ , must come from the double carbonyl-group, as the acid no longer contains that group. Supposing the alkyl constitution to be correct, one of these groups must be a methyl- and the other a propyl-group, as if both were ethyl-groups a monobasic acid could not be formed without elimination of another atom of carbon, and the presence of the fourth oxygen-atom in the acid,  $C_{17}H_{14}O_4$ , points to the second alkyl-group being isopropyl, which in the oxidation is converted into the group  $C(OH)Me_2$ . The fact that the dicarboxylic acid,  $C_{15}H_8O_5$ , does not form an anhydride, nor give a fluorescein with resorcinol, whilst the tricarboxylic acid,  $C_{15}H_{10}O_6$ , does form a fluorescein, proves that the two alkyl-groups are not in the ortho-position to one another, but that one of them is in that position to a carbon-atom of a benzene nucleus, which is joined to a carbonyl-group. From a careful survey of the above facts, and the known properties of these bodies, the authors propose the following constitutional formulæ:—



The para-position of the methyl- and propyl-groups is not proved, but from the frequency with which this combination occurs in nature, it appears probable. It is also possible that the propyl may originally be present as normal propyl, and be converted into the iso-compound during the oxidation to  $C_{17}H_{14}O_4$ .

L. T. T.

**Camphor.** By H. GOLDSCHMIDT and R. KOREFF (*Ber.*, 18, 1632—1635).—Goldschmidt and Zürrer showed that the anhydride of camphoroxime,  $C_{10}H_{15}N$ , is converted by boiling with alcoholic potash into ammonia, and the compound  $C_{10}H_{16}O_2$ , which was regarded as a carboxylic acid, and named campholenic acid (*Abstr.*, 1884, 1364). Kachler and Spitzer obtained the same compound from  $\beta$ -dibromocamphor, but they regard it as a hydroxycamphor (this vol., p. 173). According to the view held by the authors, the anhydride of camphor-



oxime must be the nitrile of campholenic acid, and the experiments described support this view. The conversion of the compound  $C_{10}H_{15}N$  into an amidoxime was previously mentioned. It also reacts with aniline and paratoluidine hydrochlorides, with formation of phenylcamphenylamidine,  $C_9H_{15}C(NH_2) : NPh$ , and paratolylcamphenylamidine,  $C_9H_{15}C(NH_2) : NC_7H_7$ , respectively, the latter compound crystallising in lustrous white needles melting at 114–115°.

On reducing the compound  $C_{10}H_{15}N$ , four atoms of hydrogen are taken up, and a base,  $C_{10}H_{19}N$ , obtained, the platinochloride of which has the formula  $(C_{10}H_{15}N)_2 \cdot H_2PtCl_6$ .

Camphor reacts both with free hydroxylamine and (although not so readily) with the hydrochloride; monobromocamphor does not react with hydroxylamine hydrochloride, and remains nearly unchanged after several days' heating at 180°; monobromocamphor yields camphoroxime when heated with free hydroxylamine, the latter apparently reducing the monobromocamphor to camphor.  $\alpha$ -Dibromocamphor gives no reaction with hydroxylamine hydrochloride, and  $\beta$ -dibromocamphor could under no conditions be made to yield an acetoxime. A. K. M.

**Reactions of the Glucosides, Helicin, and Glucovanillin.** By F. TIEMANN and A. KEES (*Ber.*, **18**, 1657–1665).—These glucosides give reactions characteristic of the aldehydes; their aqueous solutions are coloured reddish-violet by a colourless solution of rosaniline in sulphurous acid, whilst glucosides, such as salicin and coniferin, do not show the reaction. When an alkaline solution of paradiazo-benzenesulphonic acid is added to an aqueous solution of helicin, and then a grain of sodium amalgam, a red, and afterwards a reddish-violet coloration, appears in about five minutes; glucovanillin gives the same result, although more slowly. Salicin and coniferin yield the same coloration, but only after about 15 minutes (comp. Abstr., 1883, 829). Helicin and glucovanillin also yield compounds with hydrogen sodium sulphite, which are readily soluble in water and difficult to purify.

The *phenylhydrazine-derivative of helicin*,



is readily soluble in alcohol, ether, and hot water, nearly insoluble in cold water, and is insoluble in benzene. It separates from its aqueous solutions as a white mass, which, on drying, becomes brown and melts at 187°; it does not reduce Fehling's solution. It is converted by emulsin into grape-sugar and orthohydroxybenzylidene-phenylhydrazine,  $HO \cdot C_6H_4 \cdot CH \cdot N_2HPh$ . The *phenylhydrazine-derivative of glucovanillin*,  $C_6H_3(CH \cdot N_2HPh)(OMe) \cdot O \cdot C_6H_{11}O_5$  [1 : 3 : 4], forms a white mass, very sparingly soluble in cold water and in ether, readily in alcohol, and insoluble in benzene. It becomes brown when exposed to the air, melts at 195°, and yields a green precipitate with Fehling's solution, which dissolves on heating without separation of cuprous oxide. It is converted by emulsin into grape-sugar, and the *phenylhydrazine-derivative of vanillin*,  $HO \cdot C_6H_3(OMe) \cdot CH \cdot N_2HPh$ , which, for comparison, the authors have also prepared from vanillin; it forms silvery-greyish white scales melting at 105°, dissolves readily

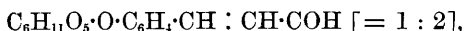
in alcohol, ether, and benzene, and very sparingly in water and light petroleum.

*Helicinaldoxime*,  $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH : NOH$ , forms slender white needles, melting at  $190^\circ$ , and containing 1 mol.  $H_2O$ . It is moderately soluble in water, less so in alcohol, and insoluble in ether, very readily soluble in acids and alkalis. It gives no characteristic colour-reaction with sulphuric acid, and is not reduced by Fehling's solution at a gentle heat. Its aqueous solutions are strongly laevorotatory. Emulsin converts helicinaldoxime into grape-sugar and salicylaldoxime.

*Glucovanillinaldoxime*,  $C_6H_{11}O_5 \cdot O \cdot C_6H_3(OMe) \cdot CH : NOH$ , forms slender, mostly yellow-coloured needles, melting at  $152^\circ$  and containing 1 mol.  $H_2O$ . It is less soluble than helicinaldoxime in water and alcohol, and is insoluble in ether. With dilute acids, alkali, concentrated sulphuric acid, and Fehling's solution, it behaves exactly like the helicin-derivative, and its aqueous solutions are likewise strongly laevorotatory. By emulsin, it is converted into grape-sugar and vanillinaldoxime; the latter is identical with the compound prepared by Lach directly from vanillin (Abstr., 1883, 1104); its melting point is, however, found by the authors to be  $121-122^\circ$ .

By means of the above reactions, helicin and glucovanillin can be detected even in dilute aqueous solutions and in the presence of other glucosides, which do not contain an aldehyde-group united to an aromatic nucleus. A. K. M.

**Glucosides prepared from Helicin.** By F. TIEMANN and A. KEES (*Ber.*, 18, 1955—1969).—*Gluco-orthocoumaraldehyde*,



is prepared by heating helicin with acetaldehyde, the mixture being made feebly alkaline. It crystallises in slender needles containing 1 mol.  $H_2O$ , is generally pale yellow, but white when pure; it melts at  $199^\circ$ . The phenylhydrazine-derivative forms a voluminous white mass and melts at  $130-132^\circ$ . *Gluco-orthocoumaraldoxime*,



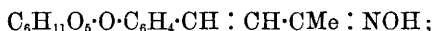
prepared by the action of hydroxylamine hydrochloride on the aldehyde, forms long white needles, melts at  $230^\circ$ , is soluble in alcohol, more readily in hot water, insoluble in ether.

*Orthocoumaraldehyde*,  $HO \cdot C_6H_4 \cdot CH : CH \cdot COH$ . Gluco-orthocoumaraldehyde is only slowly decomposed by dilute acids into dextrose and resinous products; but under the influence of emulsin it is resolved into dextrose and orthocoumaraldehyde. This crystallises in slender needles, melts at  $133^\circ$ , is readily soluble in alcohol and ether, nearly insoluble in cold water, has a faint aromatic odour, gives a dirty red coloration with ferric chloride, and dissolves in concentrated sulphuric acid with yellow colour; it readily resinifies on addition of small quantities of acids or alkalis to its aqueous solution.

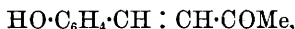
*Gluco-orthocoumaryl alcohol*,  $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH : CH \cdot CH_2 \cdot OH$ , is obtained by the action of sodium amalgam on the aldehyde suspended in water. It crystallises with 1 mol.  $H_2O$  in slender white needles, melts at  $115^\circ$ , and is readily soluble in alcohol, insoluble in ether. Emulsin

resolves it into dextrose and *orthocoumaryl alcohol*, an oil, readily soluble in alcohol, ether, and benzene, sparingly soluble in water, and which gives a red coloration with sulphuric acid.

The ketone,  $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH : CH \cdot COMe$ , is prepared by heating helicin with acetone. It crystallises with 1 mol.  $H_2O$  in pale yellow needles, melts at  $192^\circ$ , and is sparingly soluble in water and alcohol. The aqueous solution is dextrorotatory. It gives a voluminous white precipitate when mixed in aqueous solution with phenylhydrazine hydrochloride and sodium acetate. With hydroxylamine hydrochloride, it gives the *ketoamine*

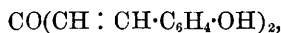


this crystallises in slender white needles, melts at  $173^\circ$ , and is sparingly soluble in water and alcohol, insoluble in ether. Emulsin decomposes the ketone into dextrose and the ketone



which crystallises in long white needles, melts at  $139^\circ$ , and is readily soluble in alcohol and ether, sparingly in water.

The ketone  $CO(CH : CH \cdot C_6H_4 \cdot O \cdot C_6H_{11}O_5)_2$  is formed, together with the preceding compound, by the action of helicin on acetone in presence of dilute alkalis. It crystallises with 4 mols.  $H_2O$ , melts at about  $257^\circ$ , is nearly insoluble in water and ether, sparingly soluble in boiling alcohol, and gives a cherry-red solution with sulphuric acid. Emulsin scarcely acts on this glucoside; long digestion with dilute sulphuric acid converts it into dextrose and a ketone,



a yellowish-brown powder melting at  $160^\circ$ .

A. J. G.

**Opionin.** By O. HESSE (*Annalen*, **228**, 299—300).—*Opionin* is contained in small quantities in Smyrna opium. It is obtained by treating opium with milk of lime at the ordinary temperature. The solution is slightly acidified with acetic acid, and evaporated until its volume is equal to that of the opium used. A brown mass is deposited from which the opionin is extracted with ammonia, reprecipitated by acetic acid, and recrystallised from alcohol or ether. The substance forms white needle-shaped crystals which melt at  $227^\circ$ . It does not evolve ammonia when heated with soda-lime. Opionin is insoluble in water, but dissolves in alkalis. It is decomposed by boiling with milk of lime, an acid being formed which is freely soluble in water and ether. Lead acetate produces a bulky precipitate with the acid in alkaline solutions.

A second acid is formed by fusing opionin with potassium hydroxide. This substance is named *opionylic acid* by the author. It is deposited from ethereal solutions in thick prisms melting at  $126^\circ$ , and dissolves freely in water. With silver nitrate, a neutral solution gives an amorphous precipitate which soon becomes crystalline. It also yields a precipitate with lead acetate after the addition of ammonia.

W. C. W.

**Oxyquinoterpene.** By C. LIEBERMANN (*Ber.*, **18**, 1803—1809).—In his research on the quinovic group (*Abstr.*, 1884, 1191), the author mentioned under the above name a substance obtained by Giesel, to which he gave the provisional formula  $C_{30}H_{46}O_2$ . Hesse (next Abstract) is inclined to regard this substance as identical with his cinchol. The author has further examined this substance, and found that it undoubtedly belongs to the cholesterin-group, and therefore proposes to substitute the name *cholestole* for that of oxyquinoterpene.

Cholestole gives the colour reaction with chloroform and sulphuric acid which is characteristic of the cholesterin-group. The author has especially compared cholestole with cholesterin, with the following results:—

	Cholestole.	Cholesterin.
Water of crystallisation	1 mol.	1 mol.
Melting point. ....	139°.	145–146°.
Crystallises from absolute alcohol. ....	In long needles .....	In micaceous scales.
Crystallises from dilute alcohol.	In micaceous scales, which cannot be reconverted into the needles.	In micaceous scales.
Crystallises from glacial acetic acid.	In scales .....	In needles which are immediately converted into scales when moistened with alcohol.
Rotation .....	$[\alpha]_D = -39 \cdot 2^\circ$ .	$[\alpha]_D = -37 \cdot 7^\circ$ .
Benzoyl-derivative. ....	Silvery scales melting at 144°.	Silvery scales melting at 149–153°.
Acetyl-derivative ....	Silvery scales melting at 124–126°.	
Bromo-derivative. ....	Unstable dibromide (?) which when recrystallised from a mixture of alcohol-ether lost hydrogen bromide, and formed white needles, which gave numbers approximately correct for a monobrominated derivative.	Dibromide crystallising easily in silky needles which melt with decomposition at 113–114°.

At present the author is inclined to think that cholestole belongs to the cholesterin-group, and its formula lies between that of cholesterin,  $C_{26}H_{44}O$ , and that of cinchol,  $C_{20}H_{34}O$ . Of this group of compounds, it seems most closely to resemble capreol.

A good reaction for the cholesterin-group (including cholestole) is the following. The substance is dissolved in just sufficient acetic anhydride for solution in the cold, and then pure concentrated sulphuric acid is dropped slowly in. A red coloration is produced which, however, soon disappears (especially if a drop or two more sulphuric be added), and is replaced by a tolerably permanent blue coloration.

L. T. T.

**So-called Fat or Wax from Cinchona Bark.** By O. HESSE (*Annalen*, **228**, 288—298).—The existence of a fatty substance in

cinchona bark has been noticed by Lauber, Reichardt, Reichel, and Flückiger. Kerner succeeded in obtaining a crystalline compound, which he termed cinchocereotin. This substance was afterwards examined by Helms (*Archiv f. Pharm.*, **221**, 229), who ascribed to it the composition  $C_{27}H_{48}O_2$ . The author finds that this substance is really an isomeride of quebrachol (Abstr., 1882, 744), and does not belong to the same class of compounds as betuline and cerine, as Helms supposed. It is best prepared by extracting the bark with low boiling petroleum. The extract is evaporated and the residue dissolved in hot alcohol and boiled with charcoal. On cooling, a small quantity of a green amorphous substance is deposited. After this has been removed by filtration, the solution is allowed to evaporate at the ordinary temperature until it deposits crystals.

By this process the compound *cupreol*,  $C_{26}H_{34}O + H_2O$ , is obtained from *China cuprea*, in which it occurs to the extent of 0.002—0.005 per cent. It is also found together with *cinchol* in the bark of *Cinchona officinalis*, and in *C. calisaya*, var. *Schuhkkräft*. Cupreol bears a close resemblance to quebrachol. It is deposited from alcoholic solutions in glistening plates containing 1 mol.  $H_2O$ , and from ether or light petroleum in anhydrous needle-shaped crystals. The hydrated crystals lose a portion of their water of crystallisation at  $25^\circ$ . The solution in chloroform is laevogyrate,  $[\alpha]_D = -37.5^\circ$ . The solution in chloroform gives a blood-red coloration with sulphuric acid. The *acetate* crystallises in plates (m. p.  $126^\circ$ ), freely soluble in chloroform, ether, and hot alcohol. The *propionate* melts at  $111^\circ$ , and in other respects resembles the acetate.

*Cinchol*,  $C_{26}H_{34}O + H_2O$ , occurs in all true cinchona barks, but is not found in *China cuprea*. It is most abundant in the bark of *Cinchona calisaya*, var. *Ledgeriana*. It is deposited from alcohol in crystalline plates containing 1 mol.  $H_2O$ . The water of crystallisation is partially driven off at  $25^\circ$ . The anhydrous substance melts at  $139^\circ$ , cupreol melts at  $140^\circ$ . The chloroform solution is laevogyrate,  $[\alpha]_D = -34.4^\circ$ . The *acetate* is deposited from alcohol in white needles which melt at  $124^\circ$ . The *propionate* forms a white powder composed of microscopic plates; it melts at  $110^\circ$ . There is a close resemblance between cupreol, cinchol, and quebrachol; according to the author, these three compounds belong to the class of cholesterins, and cinchol is identical with Liebermann's oxyquinoterpene. W. C. W.

**Cochineal and Carmine.** By C. LIEBERMANN (*Ber.*, **18**, 1969—1975).—The statements occurring in the text-books as to the composition of cochineal are very incorrect. The author finds that the amount of pure colouring matter present cannot much exceed 9—10 per cent., whilst it is usually stated as forming from 26—50 per cent. of the insect; the statements as to the amount of fat are equally incorrect.

A sample of pure carmine was obtained and investigated; when heated at  $100^\circ$  it lost 17 per cent. of water, but slowly recombined with water, absorbing about 14—15 per cent. on exposure to the atmosphere. It contained 3.7 per cent. of nitrogen, of which only 0.25 per cent. was eliminated as ammonia when boiled with dilute

aqueous alkalis. By boiling carmine with dilute sulphuric acid, a small quantity of basic nitrogenous substance was obtained. It has been suggested that the colouring matter of cochineal is a glucoside, but the results obtained negative the assumption. The dried carmine yielded 8.1 per cent. of a white ash containing—

SnO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	Total.
0.67	43.09	44.85	1.02	3.23	3.56	3.20	99.62

and also traces of Fe, Cu, and SiO<sub>2</sub>.

In an ammoniacal solution of carmine neither the aluminium nor calcium can be detected by the usual reagents. A. J. G.

**New Isomeride of Euxanthone.** By A. BISTRZYCKI and S. v. KOSTANECKI (*Ber.*, **18**, 1983—1988).—Recent researches have shown it to be probable that euxanthone is a dihydroxydiphenylcarbrolactone (dihydroxydiphenyleneketone oxide); it was thought that the condensation of resorcylic acid might yield euxanthone; the substance obtained proved, however, to be an isomeride.

*Isoeuxanthone*, C<sub>15</sub>H<sub>8</sub>O<sub>4</sub>, is prepared by distilling dried resorcylic acid (1 part) with acetic anhydride (1½ parts); it crystallises in small, very pale-yellow needles, melts at 243°, is insoluble in water, moderately soluble in ether, readily soluble in alcohol, alkalis, and concentrated sulphuric acid; all the solutions are yellow, but of less intense colour than those of euxanthone. It gives a greyish-green coloration with ferric chloride, and a pale-yellow precipitate with lead acetate. When magnesium sulphate is added to a boiling ammoniacal solution of isoeuxanthone, a thick, clear yellow precipitate is obtained.

The mother-liquor from the recrystallisation of isoeuxanthone contains a substance which separates in flocks on diluting it with water. This dissolves in aqueous soda with blue fluorescence, and gives a green fluorescent solution on treatment with sodium amalgam.

A dihydroxyphenylcarbrolactone containing both the hydroxyl-groups in the same benzene nucleus should be obtained by heating salicylic acid with phloroglucinolcarboxylic acid and acetic anhydride; the product of the reaction was found not to be identical with euxanthone, and was not further examined.

*Ditolylcarbrolactone*, C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>, is obtained by distilling parabromosalicylic acid with acetic anhydride; it crystallises in yellow needles and melts at 143°. Its solution in concentrated sulphuric acid has a bluish-green fluorescence.

By heating resorcinol (20 parts), hydrogen potassium carbonate (100 parts), and water (200 parts) in a reflux apparatus for one and a half hours, a much better yield of resorcylic acid is obtained than by the method with ammonium carbonate. The authors find the melting point of the acid to be 213°; it has been variously stated at 194—206°.

A. J. G.

**Action of Halogens on Pyrroline in the Presence of Caustic Alkalis.** By G. CIAMICIAN and P. SILBER (*Ber.*, **18**, 1763—1767).—In continuation of their previous work (*Abstr.*, 1884, 1367), the

authors find that by reducing the quantity of active chlorine of the sodium hypochlorite solution from 25 grams (in previous Abstract wrongly given as 50 grams) to 15 grams per litre (*i.e.*, to 10 grams pyrroline), dichloromaleic acid was alone formed. By increasing the chlorine to 45 grams in  $\frac{1}{2}$  litre to 10 grams pyrroline, dichloroacetic acid was almost the only product. Pseudacetopyrroline gives almost the same results as pyrroline.

Bromine acting on pyrroline in alkaline solution yields almost exclusively dibromomalënimide. But when bromine acts on a plain aqueous solution of pseudacetopyrroline, tribromacetopyrroline,  $C_6NH_4OBr_3$ , is formed which crystallises in silky needles, melts at  $179^\circ$ , and is insoluble in water, but soluble in most other solvents. It is easily converted into the pentabrominated derivative,  $C_6NH_2OBr_5$ , when heated with bromine in acetic solution.

When iodine acts on pyrroline in the presence of alkalis, tetriodopyrroline (Abstr., 1883, 350) is produced. L. T. T.

**Constitution of Synthetical Pyridine-derivatives and of Iso-cinchomeronic Acid.** By A. HANTSCH (*Ber.*, 18, 1744—1749).—The author has already shown (Abstr., 1884, 1193) that in substituted pyridine-derivatives obtained by the condensation of ammonia with aldehydes and ethyl acetoacetate, the alcohol radicle derived from the aldehyde was found in the para- (or  $\gamma$ -) position to the nitrogen-atom. It seemed probable that in trialkylised pyridinedicarboxylic acids thus obtained the remaining two alkyl-groups would occupy the ortho- (2 : 6), the carboxyls the meta- (3 : 5) positions. Ladenburg and Roth's recent research (this vol., p. 815) has removed the last doubt that isonicotinic is the  $\gamma$ -acid. The trimethylpyridinedicarboxylic acid from ammonia acetaldehyde and ethyl acetoacetate forms when oxidised a dimethylpyridinetricarboxylic acid, which in its turn yields Ladenburg and Roth's  $\alpha$ - $\gamma$ -lutidine. This proves that one of the methyl-groups must be in the  $\alpha$ -position. In a research which has not yet been published, Epstein, by employing an aldehyde containing an easily oxidisable alcohol radicle, has obtained a trialkylated pyridinedicarboxylic acid, in which the  $\gamma$ -alkyl radicle must be first affected by oxidation. The tricarboxylic acid obtained by oxidation yields a lutidine which differs from the above  $\alpha$ - $\gamma$ -lutidine, and is undoubtedly a 2 : 6 dimethylpyridine. For the formation of any but a 2 : 6 or 2 : 4 lutidine would necessitate one of the original carboxyls being in the  $\alpha$ -position, and if so, analogy with other pyridinecarboxylic acids shows that this would be the first carboxyl-group to be eliminated. But, as is known, collidinedicarboxylic acid yields a monocarboxylic acid, which on oxidation forms a tetracarboxylic acid, identical with that obtained from flavoline (this vol., p. 400), and therefore has the constitution [2 : 3 : 4 : 6]. It is therefore clear that no carboxyl can have been split off from the 2 or 6 position, and that these positions must originally have been occupied by alkyl-groups. There can, then, be no doubt that the constitution of the trimethylpyridinedicarboxylic acid from ammonia, aldehyde, and ethyl acetoacetate is  $C_5NMe_3(COOH)_2$  [Me : COOH : Me : COOH : Me = 2 : 3 : 4 : 5 : 6].

Epstein's lutidine when oxidised yields an acid identical with the isocinchomeronic acid obtained by Weidel and Herzig from the lutidine from tar. It is thus clear that isocinchomeronic acid must be the 2 : 6 acid, and not, as previously supposed, a 2 : 5 or 3 : 5 acid. The author's acid, when distilled, decomposes almost entirely into pyridine and carbonic anhydride, and only yields a trace of monocarboxylic acid, which appears to be picolinic, and certainly is not nicotinic acid. The author considers that the nicotinic acid obtained by Weidel and Herzig from their acid was due either to the presence of another isomeric acid (or possibly of nicotinic acid) as an impurity.

L. T. T.

**Methylquinolines.** By O. DOEBNER and W. v. MILLER (*Ber.*, **18**, 1640—1646).—Only two methylquinolines are well known which contain the methyl-group in the pyridine nucleus, namely, the  $\alpha$ -compound or quinaldine, and the  $\gamma$ -compound or lepidine. According to Riedel (*Abstr.*, 1883, 1152),  $\beta$ -methylquinoline may be obtained from methylhydrocinnamic acid, but his results do not agree with those obtained by the authors. It was previously shown (*Abstr.*, 1884, 1376) that the base ( $\alpha$ -ethyl- $\beta$ -methylquinoline) obtained from aniline and propaldehyde is converted by oxidation into a methylquinolinecarboxylic acid which, by the elimination of carbonic anhydride, yields a base, then thought to be  $\beta$ -methylquinoline, and which is now characterised as such. The  $\alpha$ -ethyl- $\beta$ -methylquinoline is oxidised by means of chromic mixture into  $\beta$ -methylquinolinecarboxylic acid, crystallising in nodular clusters of crystals, melting at 143—144°. When this is heated at 160°, carbonic anhydride is eliminated, and  $\beta$ -methylquinoline,  $C_9H_8NMe$  [ $Me = 3'$ ], distils over as a yellow oil, which after repeated fractioning boils constantly at 250° under 710 mm. pressure. When cooled by a freezing mixture, it solidifies to a white crystalline mass melting at 10—14°. The *platinochloride*,  $(C_{10}H_9N)_2, H_2PtCl_6 + 2H_2O$ , *aurochloride*,  $C_{10}H_9N, HAuCl_4$ , *picrate*,  $C_{10}H_9N + C_6H_3N_3O_7$ , *methiodide*,  $C_{10}H_9N, MeI$ , and *amyliodide*,  $C_{10}H_9N, C_5H_{11}I$ , are described. A small quantity of a secondary product was also obtained on heating  $\beta$ -methylquinolinecarboxylic acid. It has a higher boiling point than  $\beta$ -methylquinoline, crystallises in long colourless needles melting at 145°, is insoluble in water, somewhat soluble in ether, and readily in alcohol. It is probably a dimethyl-diquinoline,  $(C_{10}H_8N)_2$ ; its *platinochloride*,  $C_{20}H_{16}N_2, H_2PtCl_6$ , is described.

By the oxidation of  $\beta$ -methylquinoline with chromic acid,  $\beta$ -quinolinecarboxylic acid,  $C_9NH_7COOH$  [ $COOH = 3'$ ], is obtained, identical with the acid obtained by Graebe and Caro from acridinic acid (*Abstr.*, 1880, 398), and by Riedel by the oxidation of  $\beta$ -ethylquinoline (*loc. cit.*). The base from which the authors obtained it is therefore without doubt  $\beta$ -methylquinoline.

The  $\alpha$ -,  $\beta$ -, and  $\gamma$ -methylquinolines and some of their derivatives are compared in the following table:—



	$\alpha$ -compound.	$\beta$ -compound.	$\gamma$ -compound.
Base .....	b. p. 240°.	b. p. 250°.	b. p. 256°.
	m. p.	m. p.	m. p.
Picrate .....	—	187°	207—208°
Methiodide .....	195°	221	173—174
Ethiodide .....	232	—	141—143
Amyliodide .....	—	215	158—160
Benzylidene-compound..	99—100°	—	92°
Quinolinecarboxylic acid	156°	273	256°

A. K. M.

**Adenine.** By A. KOSSEL (*Ber.*, **18**, 1928—1930).—The author has previously described this base as occurring in animal tissues and yeast (this vol., p. 566). When treated with nitrous acid, adenine is converted into hypoxanthine, to which it must therefore stand in the same relation as guanine does to xanthine. When heated with dilute acids, adenine is slowly decomposed; the products are under investigation. Adenine seems to be one of the decomposition-products of nucleïn, and is probably an intermediate product in the formation of hypoxanthine from nucleïn; it occurs in the extracts of most animal and vegetable tissues. When nucleïn is heated with dilute sulphuric acid, small quantities of adenine are formed.

A. J. G.

**Papaverine.** By G. GOLDSCHMIEDT (*Monatsh. Chem.*, **6**, 372—403).—Papaverine according to Merck has the formula  $C_{20}H_{21}NO_4$ , whilst Hesse (*Annalen*, **143**, 75, and *Supplement*, **8**, 289) attributes to it the formula  $C_{21}H_{21}NO_4$ . By the oxidation of this substance by an aqueous solution of potassium permanganate, the author obtained *veratric acid*,  $C_8H_9O_4$ , *hemipinic acid*,  $C_{10}H_{10}O_6$ , and *pyridine-tricarboxylic acid*,  $C_8H_5NO_6$ , oxalic acid, ammonia, and a new acid, *papaveric acid*, which formed the chief product.

*Papaveric acid*,  $C_{16}H_{13}NO_7$ , is a white crystalline powder melting at 233°, at the same time decomposing with evolution of gas. It is sparingly soluble in cold and hot water, and also in such solvents as ether, alcohol, benzene, &c. It is most easily dissolved by hot dilute alcohol, glacial acetic acid, or amyl alcohol. Its aqueous solutions are strongly acid, decompose carbonates, and give precipitates with lead acetate, silver nitrate, and copper acetate.

The ammonium, potassium, calcium, barium, basic copper, and normal and acid silver salts are described.

Papaveric acid dissolves in concentrated hydrochloric acid, forming a yellow solution, from which orange needle-shaped crystals separate out, having the composition  $C_{16}H_{13}NO_7 \cdot HCl + 2\frac{1}{2}H_2O$ . This solution yields a second deposit of orange-red crystals, consisting of the anhydrous hydrochloride. It does not form a platinochloride.

*Mononitropapaveric acid*,  $NO_2 \cdot C_{16}H_{13}NO_7$ , is formed by dissolving the acid in concentrated nitric acid, or by heating a solution of the acid in glacial acetic acid with nitrous acid. It is easily soluble in hot water, alcohol, and glacial acetic acid, but only sparingly soluble in cold

water. It crystallises from water in slender, lustrous, yellow needles, containing 1 mol.  $\text{H}_2\text{O}$ ; it melts at  $215^\circ$ . Its *silver* salt,



forms a white crystalline powder sparingly soluble in hot water. Together with the above nitro-acid, the production of two other compounds has been observed, one crystallising from water in yellow lustrous needles melting at  $122^\circ$ , and a red substance which is sparingly soluble in water and alcohol, melts at  $245\text{--}246^\circ$ , and has the formula  $\text{C}_{14}\text{H}_8\text{NO}_7$ .

*Pyropapaveric acid*,  $\text{C}_{15}\text{H}_{13}\text{NO}_5$ , is formed when papaveric acid is heated at  $235^\circ$ . It is more easily soluble in water and alcohol than papaveric acid, but less soluble in dilute alcohol than the latter. It crystallises in small white leaflets melting at  $230^\circ$ . Its *silver* salt is obtained as a white precipitate on adding silver nitrate to the ammonium salt.

Papaveric acid when fused with potassium hydrate yields proto-catechuic acid, and when heated with alcoholic potash yields a small quantity of ammonia. P. P. B.

**Action of Alkalis on Cinchonine and other Cinchona Alkaloids.** By A. KRAKAU (*Ber.*, 18, 1934—1935).—By heating cinchonine with caustic alkalis at  $200^\circ$  in a current of superheated steam, the author has obtained, together with quinoline and lepidine, a solid substance that remains in the fused mass, and a very viscid dextro-rotatory oil which distils with the steam. Similar products were obtained from cinchonidine. Quinidine and quinine also yield a solid substance and an oil: the latter contains a dextrorotatory and two inactive bases, one of which yields a hydrate melting at  $52^\circ$ .

A. J. G.

**Action of Chlorine and Iodine on Pilocarpine.** By CHASTAING (*Compt. rend.*, 100, 1593—1594).—When chlorine gas is passed into a well-cooled solution of pilocarpine in chloroform protected from light, the dichloride of dichloropilocarpine hydrochloride,



is obtained. It forms a soft transparent resin, which changes to lamellar crystals when left over quicklime for some weeks. These crystals have the composition  $\text{C}_{11}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_2 \cdot \text{HCl}$ , and when treated with silver oxide they yield the liquid feebly alkaline base  $\text{C}_{11}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_2$ . When chlorine acts on pilocarpine in presence of moisture, a base,  $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_2$ , is obtained. The action of light complicates the reaction, and brings about the formation of secondary products.

When a chloroform solution of pilocarpine is mixed with a solution of iodine in chloroform, the colour of the iodine disappears, and if the chloroform is evaporated, and the liquid kept in a vacuum over soda-lime, part of the excess of iodine is volatilised, and on treating the residue with silver oxide in presence of chloroform, a base of the composition  $\text{C}_{11}\text{H}_{15}\text{IN}_2\text{O}_2$  is obtained. No diiodo-pilocarpine is formed under these conditions. When a solution of pilocarpine in chloroform

is agitated in presence of light with an aqueous solution of iodine in potassium iodide, no substitution-product is formed. C. H. B.

**Examination of Humus obtained from Peat.** By L. SOSTEGNI (*Landw. Versuchs-Stat.*, **22**, 9—14).—Notwithstanding the many investigations of humous substances contained in soils and in peat, the author believes their true chemical composition to be still unknown. Mulder's analyses of many specimens of natural and artificially obtained humous substances varied between 60.13—61.43 per cent. C, 3.04—3.61 per cent. N, and 4.74—4.92 per cent. H. He therefore assumed that 40 atoms of carbon combined with different proportions of hydrogen and oxygen. The nitrogen he considered to be entirely ammoniacal, but this is doubtful, as a portion may exist as organic combinations in the humus. He also obtained a combination of humus with 2 to 6 atoms of chlorine, from which he concluded that water was decomposed, 2 atoms of chlorine and 4 of oxygen combining with the acid, 4 mols. of hydrogen chloride being simultaneously formed. These figures also appear doubtful, as the various kinds of humus are unstable bodies. When dried at the temperature employed by Mulder, 140—150°, the vapours emitted are acid, and accompanied by products of decomposition.

Detmer concludes from his researches that as humous substances decompose they become richer in ash, nitrogen, and carbon, poorer in hydrogen and oxygen.

The author experimented with peat humus, and as a result of numerous experiments found that by treatment with alcohol two substances of different chemical composition can be obtained. The portion soluble in alcohol is less bright, is dried with difficulty, and is slightly hygroscopic. He also thinks the difference between the ulmic and humic acids of Mulder, and the different humous products of Detmer, are explainable by the alcoholic treatment.

Numerous nitrogen estimations by Will and Varrentrap's method yielded an average of 2.08 to 2.20 per cent., both in the portions soluble and insoluble in alcohol. The action of chlorine was observed by suspending humic acid in water and allowing the gas to act six hours daily for eight days. The chlorine taken up varied from 30.99 per cent. to 32.3 per cent., which points to a higher molecular weight than given by Mulder. Humus obtained from sugar does not combine with more than 25 per cent. of chlorine. J. F.

**Constitution of the Albuminoids.** By A. GAUTIER (*Bull. Soc. Chim.*, **43**, 596—602).—On coagulating a solution of 100 grams of egg albumin by heat, alkali sufficient to saturate 1.53 grams of  $\text{H}_2\text{SO}_4$  is separated.

The purest albumin almost invariably yields about 0.5 per cent. of ash, which usually consists of sodium chloride and sulphate and calcium phosphate. It appears probable that these salts exist in the unaltered albumin as calcium chloride and sulphate and sodium phosphate.

A substance having all the characteristics of albumin may be prepared from blood fibrin, by digesting it with a solution of sodium

chloride and subsequently dialysing it. On examining the liquid from the dialysis, it is found that it contains soluble calcium salts, and it is therefore probable that the fibrin is transformed into albumin merely by the alteration of its salts.

Again by diluting egg albumin with 10 volumes of water and subsequently removing the excess of water either by evaporation in a vacuum at 45° or by congelation at a low temperature, an albumin is obtained containing exactly the same proportion of salts, water, and albuminous matter as the original egg albumin, but it has become so modified that it cannot be coagulated by heat and may be acidified with nitric acid without being sensibly precipitated, but by passing several bubbles of carbonic anhydride through it or by adding a drop or two of calcium chloride or sulphate solution, the albumin regains its normal properties.

From the above results, the author is led to believe that the modifications of albumin obtained by the action of heat, the addition of salts, &c., are chiefly due to alterations in the constitution of the small percentages of salts attached to the organic albuminous radical, although no doubt the dehydration of the albumin must also have a certain influence in these changes.

A. P.

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## Physiological Chemistry.

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**Casein in Milk, and on the Action of Rennet.** By W. EUGLING (*Landw. Versuchs-Stat.*, 1885, 392—405).—The addition of ammonium oxalate to milk does not precipitate the calcium salts, but if, after the addition of the oxalate, calcium chloride be added, then casein is separated and carries calcium oxalate down with it; it is considered that calcium is in a definite organic combination with casein, and this combination must first be destroyed before calcium can be separated as oxalate. The calcium albuminates in milk resemble basic salts, and are readily decomposed by acetic, lactic, and tartaric acids, but not by benzoic acid, &c. When acetic acid has been added and then ammonium oxalate, calcium oxalate may be recognised by the microscope, although the quantity of acid has been insufficient to coagulate the milk. Mineral acids, except boric and arsenious acids, act like strong organic acids; at the same time as calcium is in combination with casein as a basic salt, phosphates are carried down with the coagulum. Schreiner has stated that when milk is boiled, sulphuretted hydrogen is evolved, but Eugling is unable to corroborate that statement, as he has found the percentage of sulphur before and after boiling to be the same, although various samples of milk differ in their percentage of sulphur; the change which the author believes to occur on boiling is that a part of the phosphates dissolved by the alkaline phosphates of the serum pass by the action of heat out of the serum and combine with the casein compounds, the result

being the formation of an alkaline albuminate; consequently the milk has an alkaline reaction. This statement is supported by the results of the analysis of milk (fresh and boiled) after addition of alcohol, which separates casein, combined with a larger quantity of calcium if the milk has been boiled than when it is fresh. It is because of this rearrangement of the constituents of milk after boiling, that it becomes alkaline, and that rennet has no action on boiled milk; but if an acid be added so as to bring back the original condition by destroying the alkaline albuminate, then rennet produces its well-known effects. It is possible that the action of rennet is to hydrolyse a part of the milk albuminates, whereby its combinations with calcium phosphates are rendered less stable; in proof of this, it is stated that although calcium is not recognisable by means of ammonium oxalate in the serum produced by the addition of alcohol or sodium chloride, yet it is immediately precipitated in the serum from rennet, and as this serum has an acid reaction, it follows that an albuminate has been formed which holds the calcium phosphate in solution as an acid albuminate. Soxhlet considers that the separation of casein is accompanied by the formation of lactic acid; the author has been unable to detect this acid in the whey, but he has found several albuminoids, and prefers to consider the formation of acid albuminate by hydration as most probable.

If milk contains lactic acid (1 per 1000), the action of the rennet is more rapid, but the casein produced contains a smaller percentage of ash than it should normally, and is of a bitter taste; if the quantity of acid is more than  $1\frac{1}{2}$  per 1000, then the cheese is uneatable. In a cheese prepared under normal conditions, there is present 8.25—8.75 calcium compounds, which are present in the proportion of 1 mol. tricalcium to 1 mol. monohydrocalcium phosphate. Sometimes part of the calcium is replaced by magnesium.

E. W. P.

**Preventive Inoculation of Splenic Fever.** By A. CHAUVEAU (*Compt. rend.*, 101, 45—49).—One inoculation is sufficient to protect animals effectively against either experimental inoculation with strong virus, or spontaneous contagion. Cultivations attenuated by the action of compressed oxygen are as effective and as inoffensive as highly attenuated cultivations obtained by other methods. The more attenuated cultivations are still active and efficacious a long time after they have been prepared. It is important, in order to obtain the best preventive results, not to carry the attenuation of the virus too far; a quarter of a drop injected under the skin should be sufficient to kill a guinea-pig, this animal being the most sensitive to the action of the virus. These conclusions are based on a very large number of experiments, and the author quotes several cases where the inoculation has been applied with complete success to large herds of cattle and flocks of sheep infected with splenic fever.

C. H. B.

**Pathological Urines.** By A. VILLIERS (*Bull. Soc. Chim.*, 43, 550—552).—Alkaloids are not present in normal and healthy urine, but they are invariably to be found in urine passed by persons suffering even from slight indisposition. It is possible that if in disease

these alkaloids are formed more rapidly than they are removed by the kidneys, that they may ultimately be the cause of death, and the author considers that the beneficial action of light drinks (tisanes) in illness may be due to the removal of these alkaloids. A. P.

**Action of Antiseptics on Higher Organisms: Thymol.** By A. MAIRET, PILATTE, and COMBEMALE (*Compt. rend.*, 100, 1547—1549).—When thymol is injected into the veins of dogs, the animal dies when the dose exceeds 0.03 gram per kilo. of body weight, or even with smaller doses if the animal is not in good health. A detailed account of the symptoms is given in the original paper. Most of the functions and organs are affected. C. H. B.

**Relative Toxic Effect of the Organic and Saline Constituents of Urine.** By R. LÉPINE and P. AUBERT (*Compt. rend.*, 101, 90—92).—Two dogs of the same species and as nearly as possible the same size were taken, and into the femoral vein of one of them a quantity of urine was injected just sufficient to cause death. A second larger quantity of urine was evaporated to dryness, the residue incinerated, the ash dissolved in a volume of water equal to the volume of the original urine, and this solution injected into the femoral vein of the second dog until death resulted. With normal urine, if 60 c.c. per kilo. of the dog's weight were sufficient to cause death, a slightly larger quantity, about 65 c.c. of the solution of the ash, was sufficient to produce the same result; in other words, in normal urine, 85 per cent. of the total toxic effect is due to the saline constituents. With febrile urine, however, the results were very different. If 25 c.c. of urine per kilo. were sufficient to cause death, a much larger quantity, about 40 c.c. of the solution of the ash, was required to bring about the same effect; or, in other words, in febrile urine only 55 per cent. of the toxic effect is due to the inorganic salts. The symptoms produced by febrile urine are different from those produced by normal urine: for instance, the former may produce violent clonic convulsions, whilst the latter always kills by stopping the action of the heart. C. H. B.

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### Chemistry of Vegetable Physiology and Agriculture.

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**Alleged Elective Fermentation.** By MAUMENÉ (*Compt. rend.*, **100**, 1505—1506).—A criticism of some points in Bourquelot's paper (this vol., p. 1003).

**Fermentation of Invert-sugar.** By E. BOURQUELOT (*Compt. rend.*, **101**, 68—70).—A reply to Maumené.

**The Zymase of Jequirity.** By J. BÉCHAMP and A. DUJARDIN (*Compt. rend.*, **101**, 70).—The decorticated and bruised grains of



*Abrus precatorius* were macerated with water and the solution mixed with alcohol of 95°. The precipitate thus formed, when dried and dissolved in water, yields a limpid colourless solution with a lævorotatory power  $[\alpha]_D = -53.86^\circ$  to  $55.0^\circ$ . It is, however, a mixture, for if the solution is carefully mixed with acetic acid a precipitate resembling legumin is formed, and if this is removed and the filtrate then mixed with alcohol, the true jequirity zymase, physiologically active, and possessing phlogogenic properties, is precipitated. It is a yellowish substance, soluble in water, yielding a solution which is not coagulated by heat. It has a lævorotatory power  $[\alpha]_D = -66.8^\circ$ , and liquefies starch-paste.

The substance precipitated by acetic acid is insoluble in water, but dissolves in ammonium carbonate solution, and has a lævorotatory power  $[\alpha]_D = -51.8^\circ$ .

The three corresponding products obtained in the same way from the germinated grains have the lævorotatory powers  $[\alpha]_D = -46.96^\circ$ ,  $-58.8^\circ$ , and  $-51.5^\circ$ , respectively.

C. H. B.

**Carbonates in Living Plants.** By BERTHELOT and ANDRÉ (*Compt. rend.*, 101, 24—30).—The authors have estimated the amount of soluble and insoluble carbonates in the roots, stems, leaves, and flowers of certain plants at different stages of their growth. The free carbonic acid was expelled by boiling or by placing the plant in a vacuum. The following results were obtained:—

*Chenopodium quinoa*, May 18th.—Carbonic anhydride in the entire plant, soluble, 0.11; insoluble, 0.44; ratio of soluble to insoluble carbonates, 1 : 4; June 12th, soluble, 0.05; insoluble, 0.61. The percentages of carbonic anhydride in different parts of the plant were, root 0.05, stem 0.31, leaves 0.03, flower 0.03. The carbonates are concentrated mainly in the stem, and are almost entirely insoluble. It follows that they do not come from the soil.

In *Amarantus caudatus* the percentages of carbonic anhydride were, root 0.65, stem 0.4, leaves 0.09, the carbonates being concentrated in the root, two-thirds in an insoluble, and one-third in a soluble form. In *Rumex acetosa* the percentages were, on the whole plant, soluble 0.08, insoluble 0.21; in different parts, root 0.0, petioles and large ribs 0.27, stems and leaves 0.78, the greater proportion being insoluble. There are no carbonates in the root, and hence they are not derived from the soil. In *Tropæolum majus*, whole plant, soluble 0.82, insoluble 0.0; in *Oxalis stricta*, whole plant, soluble 0.06, insoluble 0.42.

Fresh plants contain a certain amount of free carbonic anhydride, produced by internal oxidation. The following analyses of different parts of *Chenopodium quinoa* illustrate this point.

	Root.	Stem.	Leaves.	Flowers.
Before boiling.....	0.21	0.64	0.13	0.29
After boiling.....	0.05	0.31	0.03	0.03

In the root, leaves, and flowers, the carbonic anhydride is mainly in the free state, whilst in the stem it seems to exist entirely as hydrogen carbonates.

When a plant is kept under water, the amount of insoluble and soluble carbonates increases in consequence of alcoholic and other fermentations. If the juice of a plant is boiled for about an hour, the proportion of carbonates remains practically unchanged on keeping. The amount of carbonic anhydride is also increased by the decomposition of certain principles analogous to compound ethers and orcellic acid. The proportion also sometimes increases as ebullition is prolonged. The presence of soluble hydrogen carbonates in the juices of a plant will tend to promote fermentation and oxidation.

The existence of carbonates in the tissues of plants must exert considerable influence on the ratio between the inspired carbonic anhydride and the expired oxygen. The absorption of carbonic anhydride by the carbonates, with formation of bicarbonates, will tend to diminish the amount of carbonic anhydride in the surrounding atmosphere, whilst the dissociation of hydrogen carbonates previously formed will produce the opposite effect, as will also the splitting up of substances analogous to orcellic acid.

The excess of hydrogen over that required to form water with the oxygen present, as observed by Schloesing, is contained in the plant in the form of albuminoids, and also, in certain cases, of alkaloids free from oxygen.

C. H. B.

**Composition of *Sinapis Alba* during Various Stages of Growth.** By R. HORNBERGER (*Landw. Versuchs-Stat.*, 1885, 415—417).—This most valuable paper consists for the most part of tables, showing the composition of all parts of *Sinapis alba* during growth, the examination being made every seventh day from May 19 to August 18.

E. W. P.

**Maize Heads as Fodder.** By F. SESTINI and A. DICOCO (*Landw. Versuchs-Stat.*, 22, 7—8).—The following are two analyses of heads of the maize plant deprived of the corn: they have been used for fodder in times of scarcity, but the great cost of pulverising or cutting them fine renders their use costly.

Water.....	11.50	13.75
Protein substances .....	4.25	3.75
Fatty matter.....	0.52	0.63
Carbohydrates .....	46.16	36.42
Cellulose .....	35.12	43.82
Ash.....	2.45	1.63
	<hr/>	<hr/>
	100.00	100.00
Total nitrogen } in 100 parts }	0.87	0.76
Protein matters } dry substance }	0.68	0.60
P <sub>2</sub> O <sub>5</sub> } in 100 parts { .....	3.20	3.86
CO <sub>2</sub> } ash { .....	16.40	10.60
Cl .....	5.00	3.90

J. F.

**Changes in Fodder during Ensilage.** By O. KELLNER and J. SAWANO (*Landw. Versuchs-Stat.*, 32, 57—71).

**Ensilage.** By Sir J. B. LAWES (*Agricultural Gazette*, 1885, **1**, 533, 565, 598, 629, 661, 725, 757, 789; **2**, 13, 98, 117, 141).—These articles record and discuss the results of experimental feeding of 40 milch cows during the winter of 1884–85, on a mixed diet, arranged with the object of comparing the nutritive value of clover ensilage with that of a quantity of mangels containing the same weight of dry matter. The ensilage was pitted in the summer of 1884, and consisted of 109 tons of 1st and 2nd crops of red clover without any rye-grass. The silage of the upper 4 feet weighed  $45\frac{1}{2}$  lbs. per cubic foot, and that of the lower 4 feet  $59\frac{1}{2}$  lbs. per cubic foot, mean 53·6 lbs. The daily yield of milk from each cow was weighed from February 4, 1884, and the daily rations were also weighed except during the summer when the cows were at grass. They received 4 lbs. decorticated cotton-cake daily during the whole period, and from February 4 to March 9, 1884,  $3\frac{1}{2}$  lbs. bran, 14 lbs. mixed hay and straw chaff, and 101 lbs. mangel, in addition. The bran, chaff, and mangels were gradually reduced in quantity, and altogether discontinued by the middle of May. During all this period the daily milk yield varied little, being about 30 lbs. per cow, the lowest day's yield being 27 lbs. (in February) and the highest 35 lbs. 3 ozs. (in May). The cows being well fed during the winter, no large increase in the milk occurred on their being turned out to pasture; and later on, in the hot and dry weather, the yield fell off.

In the beginning of December, the 40 cows were divided into two lots of 20 each, agreeing in the average number of weeks since calving (14–15), and in the average daily yield of milk (30–31 lbs.). Each of the 40 cows was then put upon a daily ration of 4 lbs. decorticated cotton-cake,  $3\frac{1}{2}$  lbs. (afterwards 4 lbs.) bran, hay and straw chaff mixed, 10 lbs. Twenty of the cows received in addition 50 lbs. clover silage each, and the other 20, 80 lbs. mangels each, increased to 90 lbs. when it was found that the silage from the lower layers of the pit contained more dry matter. After two or three weeks occupied in accustoming the cows to their food, weighing was commenced on December 24, 1884. After pointing out, as the result of many past experiments, that a cow in good milking condition will consume not less than 25 lbs. dry matter in her food daily, the author cites the German experiments on the digestibility of the different constituents of farm foods, and constructs the following tabular statement (p. 1089) of the mixed ration required, according to these experiments, by a cow in full milk weighing 1290 lbs.

The German calculations reckon all the dry substance of mangels as digestible; but only  $\frac{1}{5}$ — $\frac{1}{3}$  of the nitrogenous constituents ( $N \times 6\cdot25$ ) of mangels are really albuminoid, and it is important to bear this in mind in comparing roots with ensilage, in which much of the original albuminoid nitrogen appears in a non-albuminoid form after the fermentation.

The nitrogenous food being required, as shown in the above table, in far greater quantity for producing milk than for maintaining weight, it was deemed advisable to distribute the average ration of specially nitrogenous food (cotton-cake) amongst the different cows of each set in proportion to the individual weekly yield of milk. A cow yielding

5 gallons of milk per day, for example, would receive  $6\frac{3}{4}$  lbs. cotton-cake, and one yielding 2 gallons only 3 lbs. of cake.

	Dry substance.	Digestible nitrogenous substance.	Digestible non-nitrogenous substance reckoned as starch.	Total nitrogenous and non-nitrogenous substance.
	lbs.	lbs.	lbs.	lbs.
4 lbs. decorticated cotton cake .....	3·6	1·38	1·93	3·31
3·5 lbs. bran.....	3·0	0·42	1·41	1·83
3·6 lbs. hay chaff.....	3·0	0·19	1·52	1·71
7·2 lbs. oat straw chaff....	6·0	0·10	2·86	2·96
81 lbs. mangels.....	10·1	1·30	7·40	8·70
Required for sustenance of 1290 lbs. live weight ....	25·7 —	3·39 0·74	15·12 9·55	18·51 10·29
Required for 30 lb. milk....	— —	2·65 1·20	5·57 4·00	8·22 5·20
Estimated excess in food ...	—	1·45	1·57	3·02

*Composition of the Herbage and Silage.*—As regards silo No. 1, containing 1st and 2nd crops red clover, the total quantity of material introduced in the 16 weighings was 118 tons or 264,318 lbs.; and the total quantity of fresh silage removed for feeding purposes, day by day for three months, was 88 tons or 198,470 lbs. The total loss was therefore 30 tons (or 24·9 per cent.), of which, however, more than 28 tons consisted of water. The distribution of this loss, as regards water, mineral matter, nitrogenous and non-nitrogenous organic matter, deduced from analyses of the 16 samples of fresh herbage, and of 5 or 6 samples of silage from each layer of 4 feet in depth, is summarised below from the detailed tables given by the author:—

	Fresh herbage.	Fresh silage.	Loss.	Loss per cent. of fresh herbage.	Loss per cent. of each constituent.
	lbs.	lbs.	lbs.		
Water .....	212,745	149,510	63,234	23·9	29·7
Ash .....	5,262	4,398	865	0·3	16·4
N × 6·25 .....	8,625	7,922	703	0·3	8·1
Non-nitrogenous organic matter	37,686	36,640	1,046	0·4	2·8
	264,318	198,470	65,848	24·9	—

The actual loss of dry matter amounted to 2614 lbs. or 5·1 per  
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cent. of the total dry matter in the herbage, very nearly the same percentage of loss as occurred, according to an observation of the author's, in a rick of 40 tons of hay after standing two years. Weiske and Schulze, however, have reported a loss of 22—36 per cent. of the dry matter of lupins, maize, and lucerne during their conversion into silage. As regards the very large loss of water observed, evaporation from the exposed cut surfaces of the silo, and of the silage in process of being sampled, must account for most of it, and in addition it seems probable that there was a loss by drainage through the newly-constructed (brick and cement) floor of the silo. The explanation of the apparent loss of mineral matter is not very obvious: escape of soluble salts in the drainage liquid may have been the cause, or it may have been the well-known variable nature of vegetable ashes, caused by greater or less admixture of adventitious sand and dust. If drainage really occurred to an extent sufficient to carry away the deficient minerals, it is plain that some of the organic matter lost must be put down to this account also. From similar analyses of the herbage and silage of silo No. 2 containing a bottom layer of 1st crop meadow grass from four fields, a middle layer of 2nd crop red clover, and a top layer of 2nd crop grasses, the following summary is obtained:—

	Fresh herbage.	Fresh silage.	Loss.	Loss per cent. of fresh herbage.	Loss per cent. of each con- stituent.
	lbs.	lbs.	lbs.		
Water .....	130,617	121,861	8,756	4·7	6·7
Ash .....	4,533	4,420	113	0·06	2·5
N × 6·25 .....	6,857	6,318	539	0·3	7·8
Non-nitrogenous organic matter	42,952	38,342	4,610	2·5	10·7
	184,959	170,941	14,018	7·56	—

This herbage was ensiled in a much drier condition than that of silo No. 1, and the loss of dry matter by fermentation was much greater, being 9·7 per cent. of the total dry matter present, and occurring to the extent of 15·1 and 10·5 per cent. of the dry matter of the two grass layers, and only 4·1 per cent. of the dry matter of the clover layer. There was little or no loss of water by drainage from this silo, and the apparent loss of ash is fully accounted for by the difficulty of estimating the true ash apart from adventitious matter. The grass lost about 15 per cent. of its total nitrogen, and the clover only 0·25 per cent.

The only detailed analyses yet available for publication are those of the red clover silage of No. 1 silo; samples were taken on three different dates from the upper 4 feet of 2nd crop clover, and at five different dates from the lower 13 feet, representing the first crop clover, and the mean results are summarised below:—

	Per cent. of fresh silage.		Per cent. of dry matter.	
	2nd crop.	1st crop.	2nd crop.	1st crop.
Water .....	78·62	74·85	—	—
Soluble albuminoïds ....	0·35	0·60	1·64	2·36
Insoluble albuminoïds ...	1·79	1·90	8·39	7·56
(Total albuminoïd)....	(2·14)	(2·50)	(10·03)	(9·92)
Soluble ash .....	1·31	1·60	6·13	6·35
Insoluble ash .....	0·72	0·75	3·35	2·96
(Total ash) .....	(2·03)	(2·35)	(9·48)	(9·31)
Digestible fibre .....	5·39	6·42	25·21	25·56
Woody fibre.....	6·53	6·61	30·53	26·38
(Total fibre).....	(11·92)	(13·03)	(55·74)	(51·94)
Acetic acid.....	0·42	0·68	1·94	2·69
Lactic acid .....	0·96	0·93	4·52	3·71
(Total acids) .....	(1·38)	(1·61)	(6·46)	(6·40)
Soluble carbohydrates, amides, chlorophyll, &c.	3·91	5·66	18·29	22·43
	100·00	100·00	100·00	100·00
Albuminoïd nitrogen ....	0·35	0·40	1·61	1·59
Non-albuminoïd nitrogen.	0·19	0·23	0·90	0·92
Total nitrogen ....	0·54	0·63	2·51	2·51

The results, so far, do not point to any loss of woody fibre, or to any conversion of indigestible into digestible matter; on the other hand, they confirm previous observations of a loss of nitrogen and of a conversion of albuminoïds into other nitrogenous compounds presumably of no feeding value.

J. M. H. M.

### Analytical Chemistry.

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**Percentage of Oxygen in the Air.** By W. HEMPEL (*Ber.*, **18**, 1800—1803).—Kreusler has lately (*Landwirthsch. Jahrb.*, **14**, 305) published a long series of oxygen determinations of atmospheric air made during 1883–84, with an improved form of Jolly's apparatus. His results show fluctuations between 20·88 and 20·94 per cent. oxygen, the mean of 99 observations made during 1883 being 20·91 per cent. The author refers to alleged sources of error in his own and in Jolly's method, and defends the accuracy of the former. The author has made a similar set of 45 determinations from February 3rd to March 28th, with the apparatus lately described by him (*Ber.*, **18**, 267). His results show fluctuations between 20·877 and 20·971 per cent., the mean being 20·93 per cent. Morley, making daily experi-

ments in America during six months in 1880, obtained 20·949 per cent. as the mean. L. T. T.

**Analytical Studies on the Nitrogen of Ammonia and certain Amines and Amides.** By A. LONGI (*Landw. Versuchs-Stat.*, **32**, 15—56).—The author reviews in detail most of the methods of determining nitrogen in organic fluids, such as the sap and extracts of plants; those most generally used—Boussingault's, by distillation with magnesia milk, and Schlössing's, by treatment with milk of lime in the cold, under a bell-glass—he thinks are inapplicable when the fluid under examination contains amides or other easily decomposable nitrogenous substances; this is specially the case when glutamine and asparagine are present, as they are both altered by either method.

The changes which take place in animal or vegetable nitrogenous products when treated with alkalis, are mainly dependent on the temperature, the free access of air, and the duration of the treatment; the author therefore infers that the ammonia contained in such fluids would be expelled by alkaline hydroxides when kept in a vacuum at a temperature considerably under the boiling point of water, whilst the amides would remain undecomposed; he has devised an arrangement to carry out experiments with this object. A solution of pure ammonium sulphate was prepared, and experiments made by treating with sodium, barium, calcium, and magnesium hydroxides, the temperature being 38—40°, and the time 2½ hours; in that time, from 98·75 to 99·54 per cent. of the total ammonia was expelled by the first three substances, but the magnesia did not act so well; the operation was therefore continued for three hours, which sufficed to expel all the ammonia. The next point was to determine the behaviour of the reagents towards amides under similar conditions, those selected being crystallised asparagine and urea. With the first named, sodium, barium, and calcium hydroxides decomposed notable but irregular proportions, but in magnesia milk a reagent was found which did not decompose either asparagine or urea under the conditions prescribed.

The next step was to ascertain if ammonia could be determined in presence of amides. Solutions were prepared containing different proportions of ammonium sulphate and crystallised asparagine, and submitted to distillation with the magnesia milk. The results of 10 experiments were satisfactory, the whole of the ammonia from the salt being found; similar results were obtained with urea.

The author proceeds to criticise the method proposed by R. Sachsse for the estimation of amide combinations in vegetable fluids by sodium hypobromite, and the modifications introduced by E. Schulze, &c., and condemns them as unsuitable. His own method of procedure is thus described. A definite volume of a solution of urea, and half a volume of concentrated sulphuric acid are put into an Erlenmeyer flask of about 70 c.c. capacity, which is then placed in the air-bath, covered with a small funnel, and heated at 105—110° until all the water has evaporated. The temperature is then raised gradually to 180°, and continued at that until no more air bubbles are disengaged; it is then allowed to cool, the fluid with the washings of the flask and funnel are poured into the distillation apparatus; magnesia milk added, and the



author's method, as previously described, carried out; in four experiments with urea, the percentage of nitrogen found was 99.46—94.36, 98.56—98.95 of the total quantity. A more trustworthy method is however, desirable, and the author recommends his method previously described (Abstr., 1884, 364). J. F.

**Detection and Estimation of Small Quantities of Nitric Acid in the Air, Water, Soils, &c.** By A. GRANDVAL and H. LAJOUX (*Compt. rend.*, 101, 62—65).—The nitric acid is converted into picric acid by the action of a solution of phenol in sulphuric acid; this is converted into ammonium picrate, and the colour of the liquid compared with that of a solution of ammonium picrate of known strength.

The reagents required are (1) a solution of 3 grams phenol in 37 grams sulphuric acid monohydrate, and (2) an aqueous solution of potassium nitrate containing 0.936 gram per litre (1 c.c. = 0.0005 gram  $N_2O_5$ ).

A known volume  $V$  of the solution to be analysed is evaporated to dryness on a water-bath, the residue carefully mixed with excess of the phenolsulphonic solution, a small quantity of water added, then an excess of ammonia, and the solution finally diluted up to its original volume  $V$ . A certain volume of the standard potassium nitrate solution is treated in precisely the same way, and the solution of ammonium picrate thus obtained is diluted up to the same volume  $V$ . The colour of the two solutions is then compared by means of a Duboscq colorimeter. If  $H$  is the height of the column of the liquid under examination,  $H'$  that of the column of the standard liquid, and  $p$  the amount of nitric acid in the volume of standard solution taken, the amount of nitric acid  $x$  in the liquid analysed is given by the formula

$$x = p \frac{H'}{H}.$$
 The quantities of nitric acid in the two solutions should

be as nearly equal as possible, but the volume of the standard solution need not be exactly the same as  $V$ , since a correction can be easily made for the difference. It is convenient to prepare a series of standard solutions of ammonium picrate for comparison, and to select that which most closely resembles in tint the liquid under examination.

In applying this method to the estimation of nitric acid in air, about 50 litres of the latter are aspirated through 10 c.c. of water containing a small quantity of pure sodium carbonate, and the liquid treated as described. In the case of waters, only 10 c.c. need be taken.

This method gives results which are trustworthy to *at least* the fifth decimal place, and it will indeed estimate with considerable accuracy so little as 0.0000125 gram of nitric acid. C. H. B.

**Estimation of Phosphoric Acid in Agricultural Phosphates.** By E. AUBIN (*Compt. rend.*, 100, 1595—1596).—In order to avoid errors caused by the precipitation of silica, lime, magnesium fluoride, &c., with the ammonium magnesium phosphate, the author proceeds as follows:—1 gram of the powdered substance is dissolved in 10 c.c.

of hydrochloric acid, boiled for 10 minutes, mixed with 10 c.c. of a saturated solution of sodium acetate in acetic acid of 8° AB, diluted to 40—50 c.c. and again boiled. Whilst in ebullition, 2 to 3 grams of solid ammonium oxalate is gradually added, and the boiling continued for a few minutes. The precipitate is allowed to settle, filtered off, and well washed, and the filtrate after cooling is mixed with excess of ammonia and 20 c.c. of a solution of ammonium citrate to keep any iron and alumina in solution. Magnesia mixture is then added in excess ( $\text{MgCl}_2$  290 grams,  $\text{NH}_4\text{Cl}$  150 grams in 1 litre of water), and the precipitate weighed in the usual manner. The final volume of the liquid before filtration should be about 250 c.c., and this should contain 40—50 c.c. of ammonia of 22°. The presence of calcium fluoride in the phosphate does not affect the results. C. H. B.

**Estimation of Cadmium.** By A. CARNOT and P. M. PROROMANT (*Compt. rend.*, 101, 59—62).—25 c.c. of the solution, containing about 0.5 gram of cadmium, is mixed with 25 c.c. of a cold saturated solution of ammonium chloride, heated to boiling, and 50 c.c. of a cold saturated solution of microcosmic salt, previously heated to about 60° is added. The liquid is then boiled for a short time, allowed to cool, and the precipitate filtered off, washed with cold water, dried at 100°, detached from the filter-paper, and heated to full redness in a porcelain crucible. The residue is cadmium pyrophosphate, which melts if heated to bright redness. This method is rapid and the results are very accurate. If ammonium chloride be not added, the precipitation will not be quite complete, and the presence of alkaline acetates in considerable proportion also prevents complete precipitation. Free acetic acid renders the results inaccurate, the error increasing with the proportion of free acid. C. H. B.

**Quantitative Analysis by Electrolysis.** By A. CLASSEN (*Ber.*, 18, 1787—1797).—At the commencement of this paper, the author describes in detail an arrangement which, when applied to a small dynamo, enables the operator to employ at one time a large number of currents of different intensities, and thus carry out simultaneously determinations of metals requiring various strengths of current.

*Separation of Iron from Manganese.*—If a solution of manganese ammonium oxalate and a large excess of oxalate is electrolysed in the cold, no separation of manganese takes place until most of the excess of oxalate has been decomposed, and sufficient ammonium carbonate is formed to react on the double salt. If the solution be heated before being subjected to electrolysis, most of the carbonate is decomposed either by direct electrolysis or by neutralisation by the oxalic acid liberated, and thus no precipitation of manganese takes place. Therefore, in determining iron in the presence of manganese, a large excess of oxalate should be used, the solution heated to 70—80°, and a current employed which gives in the voltameter 10—12 c.c. gas per minute.

*Separation of Iron from Aluminium.*—Here care must be taken not to decompose too much of the oxalate. The electrolysis should, therefore, be carried out in the cold with a current giving, in the voltameter, 10—12 c.c. gas per minute.

*Estimation of Copper.*—The deposition of copper from an oxalate solution in the cold (*Ber.*, **14**, 1627) is very slow, requiring 10–14 hours. By maintaining the solution at 70–80°, this time may be reduced to 4–5 hours. A weak current must be employed, a single Bunsen cell being sufficient. L. T. T.

**New Reaction for Codeine.** By P. LAFON (*Compt. rend.*, **100**, 1543–1544).—If a trace of codeine is mixed with a solution of 1 gram of ammonium selenite in 20 c.c. of sulphuric acid, a beautiful green coloration is produced, which changes to reddish-brown as the acid absorbs moisture from the air, probably owing to the precipitation of selenium. A solution of sodium selenate in sulphuric acid gives the same reaction, although not quite so well as the ammonium selenite: 0.1 mgrm. of codeine gives a distinct coloration. This reaction is characteristic of codeine, and is not given by any other of the ordinary alkaloids or glucosides, except morphine, which is easily distinguished by means of other tests. C. H. B.

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## Technical Chemistry.

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**Liquid Bye-product in the Preparation of 1 . 2 . 4 Dinitrotoluene.** By E. NÖLTING and O. N. WITT (*Ber.*, 18, 1336—1338).—In the technical preparation of 1 . 2 . 4 dinitrotoluene about 7 per cent. of a liquid substance is produced, consisting of a mixture of di- and mono-nitrotoluenes. When distilled with steam, about 40 per cent. of the whole passes over, consisting of equal parts of para- and meta-nitrotoluene, with traces of the ortho-compound; by fractional distillation the pure meta-compound is readily obtained, and may be used for the preparation of metatoluidine. A. P.

**Preparation of New Colouring Matters.** (*Dingl. polyt. J.*, 256, 322—325.)—Ewer and Pick describe the preparation of dyes obtained by the condensation of tetralkylised diamidobenzophenones with phenols. The dyes are produced by the action of benzophenone chloride on phenol, or by the direct condensation of benzophenone with phenol, in which case however, a salt of amidobenzophenone must be used. The hydroxyl-group of the dyes may be converted into the corresponding amido-group, colouring matters of basic character being obtained, the sulphonic acids of which impart a violet or blue colour to wool or silk or mordanted cotton.

According to Reinherz, a red dye is obtained by heating 1 part pyrenequinone with 4—5 parts concentrated sulphuric acid at 180—210°, and fusing the disulphonic acid thus formed with caustic alkali. The sodium or potassium derivative of dihydroxypyrenequinone is produced, the aqueous solution of which gives coloured lakes with metallic chlorides or lead acetate. The same dye is formed on heating pyrene-

quinone with bromine at 90—115° in a closed vessel, and fusing the resulting dibromopyrenequinone with alkalis.

According to the *Chemische Fabrik auf Actien, vormals E. Schering*, a series of dyes may be obtained by treating the hydrochlorides of pyridine, quinoline, naphthaquinoline, anthraquinoline, and their homologues with chloriodine chloride. For instance, from quinoline yellow crystals of  $C_9H_7N, ICl$  are obtained.

Erlenmeyer has patented a process for the preparation of rosaniline dyes by the oxidation of mixtures of methylated amines with primary, secondary, or tertiary aromatic amines. For the production of pararosaniline, for example, 120 parts dimethylaniline, 465 parts aniline, and 920 parts arsenic acid (75 per cent.), or 123 parts methyl-violet, 501 aniline, and 558 arsenic acid are heated at 180°. The melt is then extracted with water, and the colouring matter precipitated by means of salt. The same materials in different proportions can also be oxidised by the aid of nitrobenzene in presence of iron filings. The next section of the patent gives processes for the preparation of violet and blue colouring matters by the oxidation of combinations of methylated amines with secondary and tertiary aromatic amines.

D. B.

**Reducing Vat for Indigo.** By COLLIN and BENOIST (*Dingl. polyt. J.*, **256**, 418).—To avoid the injurious effects which are produced by fermentation in indigo vats, the authors make the following suggestions: for a vat of 8000 litres, 16 kilos. of flour or starch are boiled in water for a few minutes, 1.6 kilos. sodium carbonate having been added previously; the paste is then brought into the vat and 8 kilos. of glucose, 5.38 kilos. soda, and 1 kilo. magnesia are added. The steeped starch granules serve as nutriment to the ferment, and simultaneously facilitate the reduction by holding the indigo in suspension.

D. B.

**Arbutin.** By J. DALMON (*Pharm. J. Trans.* [3], **15**, 659).—Coarsely powdered bearberries are boiled repeatedly with water. Tannin, &c., are removed from the extract by means of basic lead acetate, the decolorised liquid is then treated with hydrogen sulphide, and evaporated rapidly. Arbutin crystallises on cooling, and forms a sticky mass, "arbutose," containing generally 55 per cent. of arbutin, 35 of glucose, 10 of water. Arbutin is obtained from this mixture by treatment first with charcoal, and then with successive quantities of alcohol and distilled water. The author recommends "arbutose" for ordinary pharmaceutical preparations, arbutin being reserved for subcutaneous injection. Eruptions of the skin have been observed to accompany the medicinal use of arbutin.

D. A. L.

**Manufacture of Celluloid.** (*Dingl. polyt. J.*, **256**, 282).—This paper describes the production of celluloid as carried on by the *Compagnie Française du Celluloïd* at their works at Stains, with special reference to the precautions which are taken to prevent fires and explosions. For details see *Bulletin de Rouen*, 1884, 525.

D. B.

## General and Physical Chemistry.

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**Refractive Indices of Alums.** By C. SORET (*Compt. rend.*, 101, 156—157).—In this paper, the author gives corrected values for the refractive indices of ammonium gallium and potassium gallium alums, for various rays in the solar spectrum (compare Abstr., 1884, 109), and also the corresponding values for rubidium gallium, rubidium indium, caesium chromium, and caesium indium alums. The values for D are as follows :—

	<i>n<sub>D</sub></i> .
Ammonium gallium alum .....	1·46835
Potassium       "       " .....	1·46528
Rubidium       "       " .....	1·46579
"       indium       " .....	1·46381
Caesium       "       " .....	1·46522
"       chromium       " .....	1·48100

The relations between the refractive indices in the gallium and indium series are sensibly the same as in the aluminium and iron series (*loc. cit.*). The refractive index of caesium chromium alum is lower than that indicated by analogy. C. H. B.

**Relation between Refractive Power and Chemical Constitution.** By R. NASINI and O. BERNHEIMER (*Gazzetta*, 15, 59—105).—In this paper, the validity of Brühl's hypothesis of the constant increase of specific refraction for each olefinoid form of combination, or so-called double bond, is examined in the case of aromatic compounds, especially the derivatives of naphthalene. Accepting the received constitution of this compound, its specific refraction  $P \frac{n-1}{\delta}$ , should differ from the value calculated from the results of the paraffinoid compound by  $12 = 2.4 \times 5$ , whereas the difference is found to vary from 16.04 to 18.22. Similar discrepancies are noticed in the cases of cinnamic alcohol, anethoöl and styrene, whilst in the phenols and alcohols containing a phenylic group, there is gradual increase between the differences observed and those calculated from Brühl's hypothesis. These observations tend to show that this hypothesis is not rigidly exact, and that although the specific refraction increases as the atomic ratio of hydrogen to carbon decreases, yet no simple relation appears to exist between variation of atomic concentration and specific refraction. It would rather seem that for each homologous series, the atoms have a peculiar value for the specific refraction, and that the differences between corresponding members of isologous series are relative, not absolute. The experimental results are set forth in a series of tables. V. H. V.

**Spectro-photometric Observations.** By J. B. MESSERSCHMITT (*Ann. Phys. Chem.* [2], 25, 655—675).—It is remarked at the outset  
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that although numerous measurements have been made of the position of the absorption-bands of diaphanous media, yet few observers have done more than merely notice the relative extinction of light, notwithstanding this forms an important characteristic of absorption-spectra. In this paper, results are given obtained with Vogel's spectral photometer with various coloured solutions possessing a sensitive action on photographic plates (so-called sensibilisators). The method of investigation consisted in outline in dipping a silver bromide gelatine plate into a very dilute solution of the colouring matter to be examined, and comparing, by means of the instrument, the photographs obtained with those on the plain gelatin plate. Thus observations could be made of the intensity of illumination, or of the extinction coefficient, its negative logarithm. From the results, it follows that colouring matters which have a sensitive action can be divided into three classes: 1st, those whose relative absorption increases from the violet end of the spectrum, and which produce no marked difference in the photographic action, such as turmeric; 2nd, those which possess an absorptive action, extending from the violet end over the greater part of the spectrum, but have a marked sensitive maximum in the yellow bands, such as diamidoazobenzene; 3rd, those which show absorption-bands in the spectrum, and a corresponding sensitiveness to light, such as eosin and its derivatives, fluorescein, &c. The values for the intensity of illumination, and the extinction coefficient, are given in a series of tables.

V. H. V.

**Absorption-spectra of some Colouring Matters.** By C. GIRARD and PABST (*Compt. rend.*, **101**, 157—160).—This paper contains descriptions and drawings of the absorption-spectra of several of the more recently discovered colouring matters, such as Biebrich scarlet, Congo red, ponceau, and chrysoidine. Homologous compounds, or compounds which are closely related in constitution, give similar absorption-spectra. These spectra may be used as a means of detecting artificial colouring matters in syrups, wines, &c., the latter being acidified, and then agitated with amyl alcohol, which extracts the dye but does not dissolve the natural colouring matter.

C. H. B.

**Spectroscopic Study of Compounds Rendered Phosphorescent by the Action of Light or the Electrical Discharge.** By E. BECQUEREL (*Compt. rend.*, **101**, 205—210).—An historical summary.

**The Simplest Form of Induction Machine.** By J. ELSTER and H. GEITEL (*Ann. Phys. Chem.* [2], **25**, 493—495).

**Variation of Induction Machines.** By E. LOMMEL (*Ann. Phys. Chem.* [2], **25**, 678—679).

**Influence of the Chemical Nature and the Pressure of Gases on Electric Induction Machines.** By W. HEMPEL (*Ann. Phys. Chem.* [2], **25**, 487—493).

**Charge and Discharge of Secondary Batteries.** By CROVA and GARBE (*Compt. rend.*, **101**, 240—243).—The intensity of the current used for charging secondary batteries should not be too great, for if such is the case an evolution of gas commences some time before saturation is complete; this tends to disintegrate the active surface of the pile, and indicates a waste of energy.

When the accumulator is allowed to discharge, the current quickly acquires a constant intensity which is maintained up to a certain time, when the intensity falls suddenly, and then diminishes very gradually until the discharge is complete. This second feeble and varying portion of the current represents that fraction of the charge which is practically useless. If the rapidity of the discharge is great, the duration of the strong constant current is short, but the duration of the weaker diminishing current is very long, and the nonutilisable portion of the current may amount to five-eighths of the total charge. If, however, the intensity of the discharge is lower, the duration of the constant utilisable current is greatly prolonged, and a far larger fraction of the total charge is utilised.

The accumulator does not acquire a condition of equilibrium immediately after it is charged by a powerful current, but some chemical action takes place in the pile, and the E.M.F. diminishes slightly; a constant potential is, however, quickly attained.

C. H. B.

**A Standard Volt.** By A. GAFFE (*Compt. rend.*, **101**, 431—432).—The electromotive force of a silver chloride pile excited by an aqueous solution of zinc chloride varies with the strength of the solution, and also with the temperature and the purity of the zinc chloride. With well amalgamated zinc, pure fused silver chloride, and limpid solutions of pure zinc chloride as neutral as possible, a solution of a given strength will always give the same electromotive force. In order to obtain accurate results, it is necessary to work through a resistance of at least 5000 ohms.

C. H. B.

**Reproduction of Siemens' Electric Mercury Unit.** By K. STRECKER (*Ann. Phys. Chem.* [2], **25**, 456—487).—In this paper an account is given of the reproduction of Siemens' mercury unit and the comparison of the copies with the original; the effects of the keeping of the mercury, or its redistillation, as also of the retention of air-bubbles, are studied and found to be practically *nil*. Determinations are given of the variations of conductivity of the mercury with the temperature, and the value for the absolute mean coefficient obtained as compared with those of former observers. Finally, the mercury unit is compared with that of the British Association and Siemens and Halske's nickel unit.

V. H. V.

**Electrical Resistance of Copper at very Low Temperatures. Insulating Properties of Liquid Oxygen and Nitrogen.** By S. WROBLEWSKI (*Compt. rend.*, **101**, 160—161).—The author has determined the resistance of fine copper wire at 100°, the ordinary temperature, 0°, — 103°, — 146°, — 193°, and — 200° to 202°. It is found that the resistance decreases much more quickly than the absolute



temperature, and approaches zero at a temperature not very far removed from that obtained by the evaporation of liquid nitrogen in a vacuum, that is  $-200$  to  $202^{\circ}$ .

Liquid oxygen and liquid nitrogen are very perfect insulators.

C. H. B.

**Electrical Resistance of Alcohol.** By G. FOUSSEREAU (*Compt. rend.*, **101**, 243—245).—The specific resistance of different samples of commercial absolute alcohol varied from 2.47 to 3.68 megohms. When alcohol is mixed with water, the resistance of the liquid diminishes and attains a minimum differing very little from that of water, when the mixture contains only 3 per cent. of alcohol, but increases to that of water with more dilute solutions. In every case, a considerable alteration in the composition of the mixture is necessary to produce any notable change in the resistance. The differences observed with commercial alcohol are not due to the presence of varying quantities of water, but to small quantities of dissolved saline matter. The presence of 1 part sodium chloride in 2,600,000 parts of alcohol lowers the resistance in the ratio of 1 to 0.527, and the addition of potash produces a similar result. When alcohol is kept in glass vessels, its resistance rapidly diminishes, but if kept in porcelain vessels the resistance is not affected to anything like the same extent. The highest resistance observed with carefully purified alcohol, collected in porcelain vessels, was 7.031 megohms.

The resistance diminishes by 0.0145 of its value for each rise of temperature of  $1^{\circ}$  at ordinary temperatures. This variation is not proportional to that of the coefficient of internal friction, as is the case with water and saline solutions.

C. H. B.

**Work done in the Decomposition of Electrolytes.** By JAHN (*Ann. Phys. Chem.* [2], **25**, 525—538).—The author's researches have confirmed the previous observations of Joule and Becquerel, that in electrolytes the energy of the electric current is converted into heat, if the current effects no other work besides overcoming the resistance. In this case  $I\Delta = \frac{w}{\alpha}$ , in which  $I$  is the intensity of the

current,  $\Delta$  the difference of the potential,  $w$  the heat evolved in unit time, and  $\alpha$  the corresponding work equivalent. But if the current

effects additional work, then  $I\Delta > \frac{w}{\alpha}$  or  $I\Delta = \frac{w}{\alpha} + x$ . According to

the researches of Favre, Berthelot, and others, the greatest part of the energy of the current, not appearing in the form of heat, appears as chemical work; in this case the unknown  $x$  is none other than work required for the separation of the ions or  $\alpha x = Z$ , or the heat equivalent of the work effected by the current must be approximately equal to the heat of formation of the electrolyte. In this memoir, this point is examined in the case of the electrolysis of copper and zinc sulphates and water. In all these cases, the values for the constant  $\alpha$  were approximately equal ( $= 0.2395$ ), thus showing that all that portion of the energy of the current, which does not appear as heat, is converted into chemical work. Conversely, the heat of formation

of the electrolytes can be calculated from these results; the values found agree closely with Thomsen's determinations. V. H. V.

**Production of very Low Temperatures.** By K. OLSZEWSKI (*Compt. rend.*, **101**, 238—240).—The gas which is the subject of experiment is enclosed in the innermost of three concentric tubes, the two outer spaces being filled with liquid oxygen, and the whole surrounded by liquid ethylene. Very low temperatures can thus be obtained, and the author has solidified nitrogen, carbonic oxide, methane, and nitric oxide. By the evaporation of solid nitrogen under a pressure of 4 mm., a temperature as low as  $-225^{\circ}$  was obtained.

Liquid ethylene boiling under a pressure of 1 mm. has a temperature of  $-162^{\circ}$ , and remains perfectly transparent. Liquid air boiling under a pressure of 10 mm. has the temperature  $-220^{\circ}$ , and even under a pressure of 4 mm. shows no signs of solidification. A liquefied mixture of air and nitrogen, in equal volumes, has the temperature  $-220^{\circ}$  under a pressure of 13 mm., and remains liquid and transparent under a pressure of 4 mm.

Hydrogen shows no meniscus, even at  $-220^{\circ}$ , under a pressure of 180 atmos. A mixture of 2 vols. hydrogen and 1 vol. oxygen was cooled to  $-213^{\circ}$  under a high pressure. The liquid obtained was perfectly colourless, and boiled rapidly when the pressure was released, losing the greater part of its hydrogen, after which it remained liquid for some time under atmospheric pressure.

The author maintains the accuracy of the hydrogen thermometer at very low temperatures. (Compare this vol., p. 881.) C. H. B.

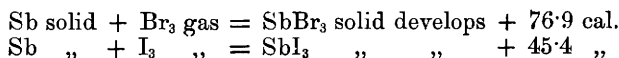
**The Use of Boiling Oxygen, Nitrogen, Carbonic Oxide, and Atmospheric Air, for Producing Cold.** By K. OLSZEWSKI (*Monatsh. Chem.*, **6**, 493—494).—A claim for priority.

**Heat of Dilution and Specific Heat of Saline Solutions.** By L. ARONS (*Ann. Phys. Chem.* [2], **25**, 408—416).—This paper contains a discussion of the formulæ theoretically deduced by Kirchhoff and Helmholtz for the heat of dilution of saline solutions. As the latter has shown that it is possible to draw conclusions regarding the heats of dilution from the variation of tension with the temperature, Babo and Wüllner's formulæ for this function are examined, but are found to be insufficient. V. H. V.

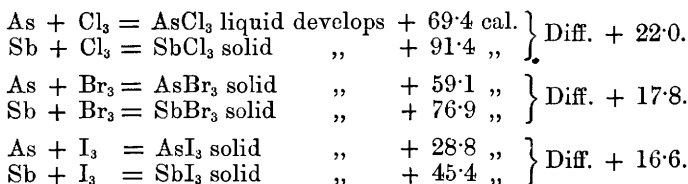
**Specific Heat of Concentrated Soda Solutions.** By A. BLÜMCKE (*Ann. Phys. Chem.* [2], **25**, 417—419).—In this paper determinations are given for the specific heat of soda solutions containing more than 50 per cent., as possessing a practical value in connection with Honigmann's soda process. The specific heat increases with the concentration until it reaches a maximum at a 73 per cent. solution, thence it decreases. This maximum value is concomitant with the best defined point of crystallisation. V. H. V.

**Heat of Formation of Antimony Bromide and Iodide.** By GUNTZ (*Compt. rend.*, **101**, 161—164).—The iodide or bromide was

dissolved in very dilute hydrofluoric acid, a corresponding amount of antimonious oxide was treated in the same way, and the quantity of heat developed in each case was determined. The following values were obtained:—



The following table gives the heats of formation of the corresponding haloïd compounds of antimony and arsenic:—

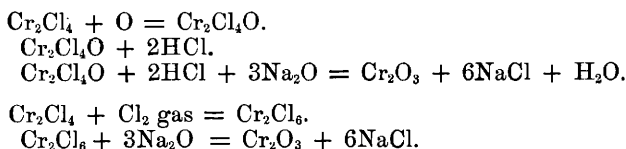


It will be observed that in the case of the solid bromides and iodides there is a difference of about 17 cal., and this would probably be also observed in the case of the chlorides if both were solid.

In Bunsen's method of estimating antimony, a dull red heat is not sufficient to convert the oxide entirely into antimonio-antimonic oxide, whilst at a bright red heat the latter is volatile.

C. H. B.

**Heat of Transformation of Chromous Chloride into Chromic Chloride.** By RECOURA (*Compt. rend.*, 101, 435—437).—By means of the following series of reactions the author has measured the heat developed by the oxidation of chromous chloride:—



The results obtained show that the combination of chlorine ( $\text{Cl}_2$ ) with chromous chloride ( $\text{Cr}_2\text{Cl}_4$ ) to form chromic chloride develops  $52.2 \times 2 = 104.4$  cal., and the combination of oxygen (1 atom) with chromous chloride ( $\text{Cr}_2\text{Cl}_4$ ) develops 100.8 cal. These values are higher than the heats of formation of many chlorides and oxides, and this fact explains the great tendency of chromous compounds to change into chromic compounds.

C. H. B.

**Heat of Formation of Alkaline Alcoholates.** By DE FORCRAND (*Compt. rend.*, 101, 318—321).—The alkali metals were dissolved in 60 equivalents of the alcohol, and the rise of temperature determined. The action of the higher homologues on lithium and sodium is so slow that exact determinations are impossible. The results obtained are given in the following table:—

	Sodium.	Potassium.	Lithium.
Methyl alcohol.....	+ 48·03	+ 50·93	+ 55·10
Ethyl alcohol .....	+ 44·70	+ 49·25	+ 51·50
Propyl alcohol.....	+ 42·35	+ 47·68	—
Fermentation butyl alcohol .....	—	+ 41·88	—
Fermentation amyl alcohol .....	—	+ 45·24	—

The two last alcohols not being normal primary alcohols, the results in these cases are not strictly comparable with the others. The values obtained with the first three alcohols closely approach those obtained by Beketoff for the action of the three metals on water, namely, Na + 43·1, K + 47·8, and Li + 48·8, but diminish somewhat as the molecular weight increases. The results confirm the author's previous conclusion (*Abstr.*, 1884, p. 143) that the water group in alcohols and acid alcohols behaves towards metals as if it were in the free state.

C. H. B.

**Heat of Formation of Picrates.** By TSCHELTZOW (*Compt. rend.*, 101, 381—383).—The author has determined the heats of formation, hydration, and dissolution of the barium, strontium, calcium, lead, magnesium, zinc, and copper derivatives of trinitrophenol (picric acid), and the numbers obtained are given in a table.

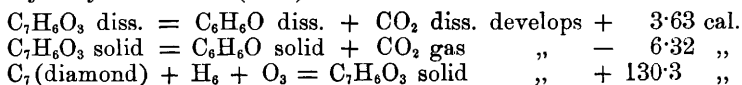
The heats of dissolution of all the hydrated salts of similar composition are practically the same. The heats of dissolution of the anhydrous salts have the same sign as in the case of the anhydrous chlorides and nitrates of the same metals. In the case of lead and barium picrates, the heat of dissolution is negative; in the other cases it is positive. The heats of neutralisation are practically the same as for nitric and hydrochloric acids, but the agreement is due to the heats of dissolution of the picric acid and its salts. The heats of formation of the solid anhydrous picrates show that the relative order of affinity of bases for picric acid is very different from that observed in the case of formic and acetic acids. Anhydrous magnesium and copper picrates are formed with a very slight development of heat, and the formation of zinc picrate is accompanied by a slight absorption of heat. It follows that these three salts will give a greater explosive effect than the other picrates under similar conditions.

C. H. B.

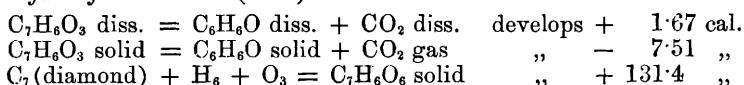
**Heat of Formation and Transformation of the Hydroxybenzoic Acids.** By BERTHELOT and WERNER (*Compt. rend.*, 101, 290—296).—The authors have determined the amounts of heat developed by the action of bromine (6 atoms) on the hydroxybenzoic acids and their sodium salts, and from the values obtained have calculated the heats of formation of the acids and the thermal disturbance corresponding with the conversion of one isomeride into another. With the ortho- and para-derivatives the reaction takes place rapidly, and the acid splits up into tribromophenol, which is precipitated, and carbonic anhydride, which remains in solution. The

meta-derivative does not decompose in this manner, but is acted on more slowly and yields a tribromo-derivative, the heat developed by the action of the bromine being almost exactly the same as that developed by its action on phenol and catechol, and not very different from that developed by the decomposition of the ortho- and para-derivatives in the manner already stated. The values obtained are as follows:—

*Hydroxybenzoic Acid (1 : 2).*



*Hydroxybenzoic Acid (1 : 4).*



It follows that the transformation of the ortho- into the para-derivative would develop +1·96 cal. if the acid was in solution, or +1·19 cal. if the acid was in the solid state. This result confirms Berthelot's earlier conclusion that the reciprocal transformation of isomerides of the same chemical function is attended by very slight thermal disturbance. This conclusion probably holds good also in the case of the meta-derivative.

The action of bromine (6 atoms) on hydroxybenzoic acid (1 : 3) (1 mol.) develops +65·04, and from this result it follows that the heat of formation of this derivative is not very far removed from that of the ortho- and para-compounds. C. H. B.

**Heats of Formation of Phthalates.** By COLSON (*Compt. rend.*, 101, 245—247).—The heats of formation of the alkaline salts were determined by direct neutralisation, and also by decomposing the salts by means of hydrochloric acid; of the lead salts, by precipitating solutions of the sodium salts with lead nitrate; of the silver salts, by precipitating solutions of the sodium phthalates with silver nitrate, and by decomposing the silver salts by means of sodium chloride. The following table gives the heats of formation of the solid salts from solid acid and solid base:—

	Orthophthalate.	Metaphthalate.	Paraphthalate.
Sodium .....	+ 31·6	+ 28·1	+ 27·0
Lead .....	+ 9·72	+ 6·85	+ 8·00
Silver .....	+ 10·03	+ 8·60	+ 11·70

In the case of the sodium salts, the values given are calculated on the supposition that the water formed remains liquid. The replacement of each atom of basic hydrogen in orthophthalic acid by sodium develops the same amount of heat. C. H. B.

**Critical Temperatures and Pressures of some Vapours.** By C. VINCENT and J. CHAPPUIS (*Compt. rend.*, 101, 427—429).—

	Critical tempera- ture. T°.	Boiling point. t°.	T - t.	Critical pressure. P.	$\frac{273 + T.}{P.}$
Hydrogen chloride ...	51·5°	- 35·0°	86·5°	96 atmos.	3·4
Methyl       "     ...	141·5	- 23·7	165·2	73   "	5·7
Ethyl       "     ...	182·5	- 12·5	195·0	54   "	8·4
Ammonia .....	131·0	- 38·5	169·5	113   "	3·6
Methylamine .....	155·0	- 2	157·0	72   "	5·9
Dimethylamine .....	163·0	+ 8	155·0	56   "	7·9
Trimethylamine .....	160·5	+ 9·3	151·2	41   "	10·5

In both series the critical temperature rises progressively, but the difference between the critical temperatures of two successive members of the series diminishes rapidly with the introduction of  $\text{CH}_2$  into the molecule. The differences between the critical temperatures and the boiling points gradually increase in the first series, but diminish in the second; the difference is not constant, as Nadejdine and Pawlewski have stated. The ratio of the absolute critical temperature to the pressure  $\frac{273 + T}{P}$  increases gradually with the complexity of the molecule, whilst the critical pressure decreases, or, in other words, for members of the same series, derivatives of the same type, the highest critical temperatures correspond with the lowest critical pressures.

Dewar has already remarked that in simple gases and typical gases under the same molecular volume, the higher critical temperatures correspond with the higher critical pressures, and the two quantities are sensibly proportional, the ratio  $\frac{273 + T}{P}$  having a constant value of about 3·5 (*Phil. Mag.* [5], **18**, 210). The authors' results confirm this conclusion so far as concerns hydrogen chloride and ammonia.

C. H. B.

**Constants of Capillarity of Saline Solutions.** By A. CHERVET (*Compt. rend.*, **101**, 235—238).

**The Symmetry and Elasticity of Crystals.** By B. MINNIGERODE (*Jahrb. f. Min.*, 1885, **1**, Ref., 380—383).

### Inorganic Chemistry.

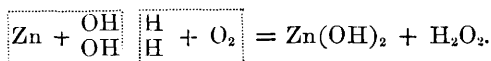
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**Co-operation of Water in the Slow Oxidation of Zinc, Lead, Iron, and Palladium-hydrogen.** By M. TRAUBE (*Ber.*, **18**, 1877—1887).—This is a continuation of the author's previous work (*Abstr.*, 1882, 795; and 1883, 150, 282, 422, 900). Zinc, lead, and iron, when

moistened with water and subjected to the action of an inclosed volume of air for 24 hours, were all acted on, and yielded precipitates of their respective hydroxides,  $\text{Zn}(\text{OH})_2$ ,  $\text{Pb}(\text{OH})_2$ , and  $\text{Fe}_4\text{O}_3(\text{OH})_6$ . When absolute alcohol was substituted for the water, the metals remained perfectly bright and unattacked, even after several months. With alcohol containing 10 per cent. of water, oxidation took place, but very slowly; with 50 per cent. alcohol, the result was the same as with pure water. Sodium retained its metallic appearance for 40 hours in *dry* oxygen, but lost it immediately a trace of moisture was admitted. The hydrogen occluded in palladium is not acted on by dry air. In this case the experimental difficulty was great, since—water being the product of any oxidation which might take place—it was necessary to remove *every trace* of water before commencing the test. A piece of palladium foil 2.15 grams in weight, and charged with about 80 c.c. hydrogen, was kept for several hours under concentrated sulphuric acid, and then introduced into an absorption-tube containing 45 c.c. air and 12 c.c. sulphuric acid, and closed by means of sulphuric acid. The volume of enclosed air remained constant for two days, but when the acid was then diluted with much water the oxygen was at once absorbed. As sulphuric acid attacks and slightly dims palladium-hydrogen, the experiment was repeated, using a syrupy aqueous solution of phosphoric anhydride containing excess of undissolved anhydride in place of the sulphuric acid. In this case also, no absorption took place until after the dilution of the acid with water. From these and other experiments already published by various investigators, there seems to be no doubt that *dry oxygen does not act on any substance at the ordinary temperature.*

When zinc was left for 12 days in contact with water which had been freed from oxygen by boiling, no trace of hydrogen or of zinc hydroxide was formed, and the metal did not lose its brightness. Lead and iron gave the same negative result, and the author has already shown (Abstr., 1883, 282) that palladium-hydrogen does not evolve any gas when kept under water freed from air. It is thus clear that the base metals have no action on pure water at the ordinary temperature.

But the moment water and oxygen are allowed to act *simultaneously* on these metals oxidation takes place, and in all these cases (with the exception of iron) hydrogen peroxide is produced. The author therefore upholds his former view of this reaction of oxidation at ordinary temperatures, which, taking the case of zinc as an example, is expressed by the equation—



The hydrogen peroxide cannot, however, accumulate, as a secondary reaction,  $\text{Zn} + \text{H}_2\text{O}_2 = \text{Zn}(\text{OH})_2$ , destroys the greater part as soon as it is formed. The fact that no hydrogen peroxide is observable when iron is being acted on is due to the very great energy of the secondary reaction with iron. This energy is well shown by the observed fact that although, when zinc is acted on by water and air, hydrogen



peroxide may be detected in a few minutes, the addition of a little iron powder to the zinc destroys all trace of the peroxide. Schönbein by employing iron-amalgam in place of iron was enabled to detect the formation of hydrogen peroxide. The oxidation of iron takes place in two stages, ferrous hydroxide being first formed, and this then further oxidised to  $\text{Fe}_2\text{O}_3(\text{OH})_6$ . This may readily be seen by placing some long pieces of wire in a test-tube filled with water. Yellowish-brown flakes of  $\text{Fe}_2\text{O}_3(\text{OH})_6$  are deposited in the upper and more exposed part of the water, whilst lower down flakes of the greenish  $\text{Fe}(\text{OH})_2$  appear. The author points out that those (base) metals which are oxidised by moist air (according to the first equation) also have the property of decomposing hydrogen peroxide according to the second equation (becoming themselves oxidised), whereas those (noble) metals which are not oxidised by moist air, decompose hydrogen peroxide into water and oxygen, but do not appropriate the oxygen. Even iron (which, as is known, does not become oxidised in an alkaline solution, such as sodium carbonate solution) decomposes hydrogen peroxide in an alkaline solution without itself being oxidised. Tin, however, forms an exception to the above rule, as it has no action whatever on hydrogen peroxide.

From a careful review of all the known facts, the author concludes that the hypothesis (held by many) of the formation of hydrogen peroxide by the oxidation of water by active oxygen is untenable. In the first place, the decomposition of the oxygen molecule would then *precede* the formation of the peroxide, and be independent of the presence of water. The above experiments show that this is not the case. Secondly, water is a non-oxidisable substance, our most powerful oxidising agents—such as permanganic acid, ozone, and the nascent oxygen liberated at the positive pole of a battery—having no action on it. Thirdly, oxygen atoms are not set free during slow oxidation, as in that case, when such easily oxidisable substances as ammonia or carbonic oxide, indigo solution, &c., are present they would be oxidised, whereas no trace of such oxidation does take place. Fourthly, during the above-described slow oxidation, easily reducible substances often give up oxygen; thus, potassium nitrate is reduced to nitrite by zinc in the presence of water and oxygen, whilst hydrogen peroxide is simultaneously formed. And, lastly, it is well known that hydrogen peroxide is not only decomposed by nascent hydrogen, but by any powerful oxidising agent, so that the presence of such an oxidising agent for the formation of the peroxide from water would also pre-determine its decomposition.

The author regards hydrogen peroxide as an “oxygen-molecule compound,” or, in other words, a reduction product of oxygen.

L. T. T.

**Slow Oxidation of Copper in Presence of Dilute Sulphuric Acid, or of a Solution of Ammonium Carbonate.** By M. TRAUBE (*Ber.*, 18, 1887—1890).—It is well known that although copper is not oxidised by moist air, it absorbs oxygen slowly when in the presence of dilute sulphuric acid. The author finds that here, as in the case of the slow oxidation of lead, zinc, iron, &c. (see last Abstract), hydrogen peroxide is formed during the reaction. It seems, therefore,

that although copper is unable to decompose sulphuric acid at ordinary temperatures, its affinity for the acid group  $\text{SO}_4$ , and that of the oxygen molecule for hydrogen, are together sufficient to cause such decomposition. The reaction is probably  $\text{Cu} + \text{SO}_4\text{H}_2 + \text{O}_2 = \text{CuSO}_4 + \text{H}_2\text{O}_2$ , and the secondary reaction,  $\text{Cu} + \text{SO}_4\text{H}_2 + \text{H}_2\text{O}_2 = \text{CuSO}_4 + 2\text{H}_2\text{O}$ . No "active" oxygen is liberated in this reaction, as carbonic oxide is not oxidised to carbonic anhydride.

The sulphuric acid in the above reaction can be replaced by ammonium carbonate, when the reactions become  $\text{Cu} + \text{CO}_3(\text{NH}_3)_2\text{H}_2 + \text{O}_2 = \text{Cu}(\text{NH}_3)_2\text{CO}_3 + \text{H}_2\text{O}_2$  and  $\text{Cu} + \text{CO}_3(\text{NH}_3)_2\text{H}_2 + \text{H}_2\text{O}_2 = \text{Cu}(\text{NH}_3)_2\text{CO}_3 + 2\text{H}_2\text{O}$ . Here again no direct oxidation by "active" oxygen can take place, as in such case the ammonium carbonate would be oxidised to nitrite.

L. T. T.

**Co-operation of Water in the Combustion of Carbonic Oxide, and Formation of Hydrogen Peroxide during such Combustion.** By M. TRAUBE (*Ber.*, **18**, 1890—1893).—Dixon has shown (*Abstr.*, 1883, 12, and *Phil. Trans.*, 1884, Part II) that a *dry* mixture of carbonic oxide and oxygen is not exploded by the electric spark, or by a glowing platinum wire, and explains the combination of a moist mixture to be due to the power of carbonic oxide to decompose water at a red heat:  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ ; and  $\text{H}_2 + \text{O} = \text{H}_2\text{O}$ . The author finds that a burning jet of carbonic oxide is extinguished when introduced into dry air, but cannot accept Dixon's explanation of the action of moisture. Hydrogen peroxide is formed during the combustion of carbonic oxide, but under ordinary circumstances is almost entirely decomposed again. If, however, the flame be allowed to impinge on the surface of water, hydrogen peroxide may be detected in this water; in one case the water contained 0.0015 per cent. peroxide. When electric sparks are passed for some hours through moist carbonic oxide no trace of carbonic anhydride is formed, so that there can be no doubt that carbonic oxide cannot decompose water at a red heat. The combustion of carbonic oxide therefore appears to take place according to the equations— $\text{CO} + 2\text{OH}_2 + \text{O}_2 = \text{CO}(\text{OH})_2 + \text{H}_2\text{O}_2$ ; and  $\text{CO} + \text{H}_2\text{O}_2 = \text{CO}(\text{OH})_2$ , the  $\text{CO}(\text{OH})_2$  being then split up into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . It is thus clear that the two molecules of water decomposed in the first stage being reformed, a mere trace of moisture is able to determine the combustion of an unlimited quantity of carbonic oxide. (See also preceding Abstracts.)

L. T. T.

**Formation of Hydrogen Peroxide during the Combustion of Hydrogen.** By M. TRAUBE (*Ber.*, **18**, 1894—1900).—When a small flame of hydrogen is allowed to impinge upon the surface of water, that water is very soon found to contain hydrogen peroxide. The author obtained the largest yield of peroxide under the following conditions:—A mixture of 64 per cent. hydrogen and 36 per cent. air was burned at the mouth of a jet formed of a glass tube of 3 mm. internal diameter, drawn out to a long conical point so as to form a very fine capillary opening; this was of such a size that under 120 mm. mercury pressure 1 litre of the mixture took 45 minutes in issuing from it. The pressure in the tube was kept at 120° mm., and the jet allowed to impinge, at an angle of 45°, on to the surface

of 200 c.c. of water in a flat basin, about one-third of the flame itself being below the general surface of the water. Under these conditions, 1 litre (measured at  $0^{\circ}$  and 760 mm.) of hydrogen yielded 0.0113 gram of peroxide. The proportion of air to hydrogen in the mixture, the size and shape of the jet, and the pressure in the tube, all have great influence on the quantity of peroxide formed. If, *with the same quantity of water*, the quantity of gas burned is increased, the hydrogen peroxide obtained does not increase in the same proportion; the gain of peroxide per litre of hydrogen consumed decreases the stronger the solution of peroxide becomes. There can therefore be no doubt that the hydrogen flame not only gives up hydrogen peroxide to the water, but also decomposes part of that which has already been absorbed. The small hydrogen flames employed had the odour of ozone, but no ozone reaction could be obtained; the author therefore concludes that the vapour of hydrogen peroxide has an odour similar to that of ozone. If sulphurous anhydride is mixed with the hydrogen, and the flame allowed as before to impinge on the surface of water, free sulphur and hydrogen sulphide are obtained, and every trace of hydrogen peroxide is destroyed. There can therefore be no "active" oxygen formed during the combustion of the hydrogen.

From a consideration of these facts the author concludes that, whether the presence of water is essential to the combustion of hydrogen or not, there can be no doubt that the reaction is similar to those already described (see preceding Abstracts). Supposing water to be essential, the reactions would be— $\text{H}_2 + 2\text{OH}_2 + \text{O}_2 = 2\text{OH}_2 + \text{H}_2\text{O}_2$ ; and  $\text{H}_2\text{O}_2 + \text{H}_2 = 2\text{H}_2\text{O}$ ; or supposing no water to be necessary in the reaction— $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$ ; and  $\text{H}_2 + \text{H}_2\text{O}_2 = 2\text{H}_2\text{O}$ . Dixon found that even with a carefully dried mixture of oxygen and hydrogen, the passage of the electric spark caused explosion, but the author points out that in Dixon's experiments the conducting wires were platinum, and that metal is known to have the property of causing the union of oxygen and hydrogen at ordinary temperatures. He therefore contends that in Dixon's experiment it is impossible to be sure of the *absolute* absence of water (a condition necessary to the decisive character of the experiment), and that it has not up to the present been determined whether the presence of water is or is not essential to the union of hydrogen and oxygen.

L. T. T.

**Transformations of Sulphur.** By D. GERNEZ (*Compt. rend.*, 101, 313–315).—A reply to Van't-Hoff (this vol., p. 1037).

**Absorption of Nitric Oxide by Ferrous Salts.** By J. GAY (*Ann. Chim. Phys.* [6], 5, 145–204).—The quantity of nitric oxide absorbed by a solution of a ferrous salt is directly proportional to the weight of ferrous iron in the solution, and is not affected by the acid combined with the iron, or by the dilution of the solution; it varies, however, with pressure and temperature. The variation for pressure is not a variation due to uniform dissociation, nor does it vary according to Dalton's law, but follows a special law, very similar to that governing the solubility of ammonia in water, apparently due to the solubility of the nitro-ferrous compound in an excess of the ferrous

solution causing a diminution in its tension of dissociation. The nitrated solution gives up the whole of its nitric oxide in a vacuum, and also in any atmosphere free from nitric oxide.

For every equivalent of nitric oxide absorbed by a solution of a ferrous salt, 10.7 cal. are disengaged. The presence of the dissolved gas augments the solubility of the ferrous salt, but on attempting to obtain crystals of the nitro-compound, it was found that although they were of a very dark colour, almost black, they contained but a very small amount of nitric oxide, very much less than that contained in the original solution. The absorption-spectrum yielded by the nitro-ferrous solution is similar for all ferrous salts, and shows one colour-band in the red and one in the green, separated by a broad absorption-band; in very concentrated solutions, or if the depth of the solution be great, the band in the green disappears. Ferrous oxide freshly precipitated by potassium hydroxide reduces nitric oxide to nitrogen, forming first magnetic oxide of iron, and finally the peroxide.

The amount of nitric oxide present in a solution of a ferrous salt of known strength may be readily determined by treating it with gold chloride; after deduction of the amount of gold precipitated by the ferrous salt the residue is the weight of metal precipitated by the nitric oxide, according to the equation  $2\text{AuCl}_3 + \text{N}_2\text{O}_2 + 3\text{H}_2\text{O} = 2\text{Au} + 6\text{HCl} + \text{N}_2\text{O}_5$ . The author considers that nitric oxide forms a definite chemical compound with the ferrous salt, and that it is not a mere case of solution. He finds the proportion of nitric oxide to the ferrous iron in a solution at 12–15° under normal pressure to be 15 of nitric oxide to 56 of iron as ferrous oxide, corresponding with the formula  $\text{Fe}_2\text{O}_2\cdot\text{NO}$ ; this result is identical with that obtained by Peligot (*Ann. Chim. Phys.* [2], 54, 17). A. P.

**Action of Direct Sunlight on a Mixture of Nitric Acid with Carbon Bisulphide contained in Sealed Tubes.** By TIFFEREAU (*Bull. Soc. Chim.*, 44, 109–110).—When 2 vols. of nitric acid and 1 of carbon bisulphide contained in a sealed tube are exposed to the action of direct sunlight, the nitric acid is decomposed, nitrous gases and hyponitric acid, with the vapour of carbon bisulphide, distil into the upper part of the tube, condensing to a greenish-blue liquid, which runs back into the carbon bisulphide; this by degrees acquires a bluish-green colour, and finally becomes almost black, whilst the layer of undecomposed nitric acid continues quite colourless and clear. After 20 to 30 days, white crystals, probably having a composition analogous to that of nitroxyl sulphate, are formed in the upper part of the tube. When the action is complete and sunlight has no further action, the tube contains two layers of transparent liquid, one quite colourless, and the other of a slightly yellowish tinge, whilst in the space above the liquids are some white cubical crystals; on one occasion the author observed the deposition of a small quantity of carbon. A. P.

**Alkaline Tetrathionates.** By N. v. KLOBUKOW (*Ber.*, 18, 1869–871).—The following modification of Fordos and Gélis' method of preparing alkaline tetrathionates by the action of iodine on the corre-

sponding thiosulphate ( $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$  (*J. pr. Chem.*, **28**, 471, and Kessler, *ibid.*, **47**, 33), overcomes the difficulty of separating the two products before decomposition of the tetrathionate sets in. The powdered *dry* ingredients are intimately mixed in equivalent proportions, and the mixture triturated with a very little water until dissolved. Small quantities of the ingredients are then alternately added to the solution until the latter is saturated, the saturation point being shown by the yellow iodine coloration. The syrupy liquid is poured into alcohol, when the tetrathionate is precipitated as a snow-white powder, whilst the iodide remains in solution. After standing for two to three hours, the precipitate may be collected, freed from iodide by washing with alcohol, dissolved in lukewarm water, and crystallised by the addition of alcohol and evaporation under reduced pressure. If the iodine coloration disappears when the syrupy liquid is poured into the alcohol, more iodine must be added until a permanent slight yellow coloration is produced, so as to insure the conversion of all the thiosulphate.

The cause of the decomposition of the tetrathionate in the older method was the heat generated in the reaction. In the present modification, the absorption of heat in the solution of the thiosulphate is greater than the evolution of heat in the reaction. A fall of temperature ( $5-8^\circ$ ) is the consequence, and this hinders the decomposition.

L. T. T.

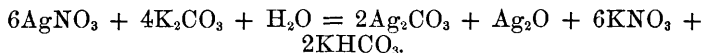
#### **Action of Potassium Permanganate on Sodium Thiosulphate.**

By M. HÖNIG (*Monatsh. Chem.*, **6**, 492).—A controversial note (compare Abstr., 1884, 151).

#### **Action of Silver Nitrate on Pure Potassium Monocarbonate.**

By E. BOHLIG (*Arch. Pharm.* [3], **23**, 381—384).—On mixing solutions of silver nitrate and potassium carbonate the silver precipitate can be obtained at will, either as a black, yellow, or pure white deposit, according to the state of concentration of the solution, and as one or the other is added in excess.

A solution of pure potassium carbonate free from hydrogen potassium carbonate was precipitated with half the amount of silver nitrate required for complete precipitation; the dark precipitate kept from the light, was filtered off, and the filtrate was examined as to the state of the remaining potassium carbonate. A portion was titrated with decinormal oxalic acid, and another portion with standard lime water and decinormal oxalic acid; the results showed the presence of potassium sesquicarbonate. The filtrate gave a white precipitate with a silver salt both before and after adding excess. The reaction with the monocarbonate is evidently as follows:—



Hence, as may be expected, the precipitated pure white silver carbonate in contact with excess of pure monocarbonate solution becomes blackened. A very sensitive test for the presence of bicarbonate is thus obtained. If the solution of carbonate gives a white precipitate with a little silver nitrate, bicarbonate is present. This is confirmed

by similarly treating another portion of the carbonate which has been previously ignited; in this case a dark-coloured precipitate is produced. J. T.

**Preparation of Magnesium.** By PÜTTNER (*Dingl. polyt. J.*, 256, 567).—Burnt magnesite, dolomite, or other magnesium mineral is intimately mixed with coal and ferric oxide, and exposed to a strong white heat in a muffle furnace. Vapours of magnesium escape and are collected and condensed in suitable receivers. D. B.

**Reduction of Metallic Solutions by Means of Gases, &c.** By G. GORE (*Chem. News*, 52, 3).—In addition to facts already given (Abstr., 1884, 393), it is shown that when magnesium is immersed in a solution of potassium cyanide, the solution is not discoloured in three days; if, however, a stream of carbonic oxide is passed through the liquid, after two days the liquid becomes brown, and the metal is coated with a black film. D. A. L.

**Crystallised Zinc Hydroxide.** By J. VILLE (*Compt. rend.*, 101, 375—378).—Very finely powdered zinc carbonate, prepared by the action of carbonic anhydride on zinc oxide in presence of water, is added gradually to a 10 per cent. solution of potash, the quantity of potash used being double that required to decompose the amount of zinc carbonate taken. In a short time, zinc hydroxide separates in prisms, which gradually increase in size. These crystals are insoluble in water, but dissolve readily in acids, and in excess of potash. Zinc hydrocarbonate may be used instead of the carbonate, but in this case the crystals are modified prisms. If a larger proportion of potash is employed, the prisms are also modified, the extent to which modification takes place increasing with the proportion of potash. This effect may be due to the action of potassium zincate, which is formed as a secondary product. C. H. B.

**Dissolution of Aluminium in Alkaline Hydroxides.** By A. CAVAZZI (*Gazzetta*, 15, 202—206).—The dissolution of aluminium in alkaline hydroxides with evolution of hydrogen, and formation of a soluble aluminate, is generally expressed by the equation  $\text{Al}_2 + 6\text{MOH} = \text{Al}_2\text{M}_6\text{O}_6 + 3\text{H}_2$ . But although the rate of the change increases with the temperature and the concentration, yet *aluminium is perfectly unaltered* by hydroxides fused so as to contain no extraneous water. On the other hand, zinc is dissolved by the hydroxides in a state of fusion, but is unaltered by boiling with their concentrated solutions. In order to throw light on the nature of these changes, the author has examined the reaction of sodium and potassium carbonates with aluminium. The metal dissolves in these solutions with evolution of hydrogen, showing that the initial change consists in the decomposition of water by the metal; the oxide produced dissolves in the alkali to form the aluminate, thus:  $\text{Al}_2 + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2$ , and  $\text{Al}_2\text{O}_3 + \text{M}_2\text{O} = \text{Al}_2\text{O}_3\text{M}_2\text{O}$ . Investigations on these points should be extended to similar cases of solution of metals or hydroxides. V. H. V.

**Separation of Didymium into its Elements.** By C. v. WILSBACH (*Monatsh. Chem.*, **6**, 477—491).—By repeated crystallisation of a mixture of the double nitrates of lanthanum and didymium with ammonium, the lanthanum salt was obtained pure, whilst the didymium salt separated into the salts of two new elements, neodymium and praseodymium.

*Neodymium*, Nd, yields salts of a splendid amethyst colour, which form rose-coloured solutions. Its oxide when strongly ignited is blue; it dissolves readily in acids and behaves as a sesquioxide of its group.

*Praseodymium*, Pr, forms green salts. Its oxide, formed by ignition of the nitrate, is dark brown; it dissolves in sulphuric acid with evolution of oxygen, and is readily reduced to a greenish-white sesquioxide when held in a reducing flame. The oxides of both elements, but especially that of praseodymium, possess the property of condensing oxygen on the surface. The atomic weights, 143·6 (for praseodymium), and 140·8 (for neodymium), are provisionally assigned to the elements. Tables of absorption-spectra are given and described. When mixed in certain proportions the elements give the original spectrum of didymium.  
N. H. M.

**Vapour-density of Thorium Chloride.** By L. TROOST (*Compt. rend.*, **101**, 360—361).—The author has determined the vapour-density of thorium chloride, and has obtained the numbers 5·90, 7·01, and 7·49. These values are obviously much nearer to 6·48, the vapour-density of a dichloride,  $\text{ThCl}_2$  ( $\text{Th} = 116\cdot2$ ), than to 12·96, the vapour-density of a tetrachloride,  $\text{ThCl}_4$  ( $\text{Th} = 232\cdot4$ ).  
C. H. B.

**Thorium Metaphosphate.** By L. TROOST (*Compt. rend.*, **101**, 210—212).—Thorium metaphosphate was prepared by fusing anhydrous thorium chloride with excess of metaphosphoric acid. It crystallises in square tables of sp. gr. 4·08 at 16·4°. These crystals belong to the rhombic system, and show a black cross with convergent polarised light; they therefore differ from the crystals of silicon metaphosphate, which belong to the regular system. They have the composition  $\text{ThO}_3\cdot 2\text{P}_2\text{O}_5$  ( $\text{Th} = 232\cdot4$ ) or  $\text{ThO}\cdot \text{P}_2\text{O}_5$  ( $\text{Th} = 116\cdot2$ ), and in this respect also are not analogous to silicon metaphosphate.  
C. H. B.

**Crystalline Basic Copper Sulphate.** By S. PICKERING (*Chem. News*, **52**, 2).—With reference to a statement that all artificially prepared basic copper sulphates had been described as amorphous powders (Shenstone, *Trans.*, 1885, 375), the author of the present note remarks that the dihydrated tetracupric salt prepared by him by the decomposition of copper sulphate by an acetate is sometimes crystalline, and has been so described (*Chem. News*, **47**, 182). The tricupric salts obtained by the author by the same method as that employed by Shenstone (*loc. cit.*), but at a lower temperature, contained a larger quantity of water, and are represented by the formulæ  $2\text{CuSO}_4\cdot 4\text{CuO}\cdot 5\text{H}_2\text{O}$ , and  $2\text{CuSO}_4\cdot 4\text{CuO}\cdot 4\text{H}_2\text{O}$  respectively.  
D. A. L.

**Alloys of Copper with Cobalt.** By G. GUILLEMIN (*Compt. rend.*, 101, 433—434).—Alloys of copper with cobalt are readily obtained by melting the two metals together under a flux of boric acid and wood-charcoal, or by melting copper with an alloy of copper and cobalt which is formed in the process of copper smelting. The alloy used by the author for this purpose had the composition Co, 48.28; Ni, 1.0; Cu, 50.26; Fe, 0.46 = 100.

The alloys investigated contained from 1 to 6 per cent. of cobalt. They have a red colour and a fine silky fracture resembling that of pure copper. They have remarkable ductility, malleability, and tenacity, and can be worked and rolled in the cold, but they cannot be tempered. They break under a tensile strain of from 25 to 36 kilos. per square mm., with an elongation of 28 to 15 per cent. An alloy containing 5 per cent. of cobalt, after forging and rolling, broke under a strain of 40 kilos. per square mm., with an elongation of 10 per cent. This particular alloy is as malleable and as little liable to oxidation as copper, and is as ductile and tenacious as iron. C. H. B.

**Action of Ammonia on the Halogen Salts of Lead.** By J. WOOD and J. L. BORDEN (*Chem. News*, 52, 43—44).—Experimenting with lead chloride precipitated from lead nitrate with hydrochloric acid, the authors find that on heating it with ammonia over a water-bath the compound  $\text{PbCl}_2 \cdot 3\text{PbO}$  is formed, whilst by keeping the mixture briskly boiling on a sand-bath, the compound  $\text{PbCl}_2 \cdot \text{PbO}$  is obtained. The latter is a creamy-yellow substance, and remains unaltered at 200°, whilst the former is much yellower, and becomes deeper yellow on heating. When lead iodide, prepared from the nitrate, is digested with ammonia in the cold, or heated with weak ammonia, it forms the oxyiodide  $\text{PbI}_2 \cdot \text{PbO}$ ; but on heating with strong ammonia more basic oxyiodides are formed, the basicity increasing with the time of digestion; for example,  $\text{PbI}_2 \cdot 3\text{PbO}$  was formed after 38 hours; and  $\text{PbI}_2 \cdot 5\text{PbO}$  after 68 hours.

D. A. L.

**Effect of Heat on Ammonium and Potassium Fluochromates.** By G. GORE (*Chem. News*, 52, 15).—The author has repeated Varené's experiments (*Abstr.*, 1881, 225) but has observed no indication of the liberation of fluorine. The platinum dish is not corroded, nor is there any evolution of gas when mixtures of ammonium or potassium dichromate and hydrofluoric acid are evaporated to dryness. The dry ammonium salt corrodes glass, and when heated in a platinum vessel is apparently decomposed according to the equation  $2(\text{NH}_4\text{F} \cdot \text{CrO}_3) = 2\text{NH}_4\text{F} + \text{O}_3 + \text{Cr}_2\text{O}_3$ . When 0.25 gram or so of the salt is heated at once, the decomposition takes place somewhat violently, evolving fumes of a slightly acid odour, which slightly discolour potassium iodide but do not affect a splint moistened with turpentine. The potassium salt undergoes a somewhat similar decomposition, the fumes evolved contain hydrofluoric acid, but neither discolour potassium iodide nor rekindle a glowing splint.

D. A. L.

**Manganites of the Alkaline Earths.** By G. ROUSSEAU (*Compt. rend.*, 101, 167—169).—The chloride of the alkaline earth is mixed



with a small quantity of the corresponding oxide and fused in a platinum crucible. As soon as the temperature reaches an orange-red heat, a quantity of manganous chloride, equivalent to half the oxide previously added, is thrown into the fused mass. Manganous oxide is thus precipitated in a finely-divided state, rapidly oxidises in contact with the surrounding air and the free base, and crystals of the manganite separate round the upper part of the crucible. In reality a manganate is first formed, and this dissociates at the high temperature. At a temperature a little above dull redness the polymanganites,  $\text{RO}, 5\text{MnO}_2$ , are formed. At bright redness dimanganites,  $\text{RO}, 2\text{MnO}_2$ , and at a still higher temperature manganites,  $\text{RO}, \text{MnO}_2$ , and bibasic manganites,  $2\text{RO}, \text{MnO}_2$ , are obtained. It would seem, therefore, that at high temperatures manganese peroxide undergoes depolymerisation similar to that observed in the case of sulphur vapour.

The compounds actually obtained by the author are  $\text{SrO}, \text{MnO}_2$ ;  $\text{SrO}, 2\text{MnO}_2$ ;  $\text{CaO}, 2\text{MnO}_2$ ; and  $2\text{CaO}, \text{MnO}_2$ . The latter forms brownish-red crystals, and its existence shows that manganous acid is tetrabasic, the compounds  $\text{RO}, \text{MnO}_2$  being acid salts.

C. H. B.

**Gold Phosphobromides and Phosphochlorobromides.** By L. LINDET (*Compt. rend.*, **101**, 164—166).—*Aurous phosphorous bromide*,  $\text{Au}_2\text{Br}_2, 2\text{PBr}_3$ , is obtained by heating phosphorous bromide with aurous bromide (prepared by heating auric bromide at  $150^\circ$ ) in sealed tubes at  $140$ — $150^\circ$ , removing the unaltered phosphorous bromide, and drying the product in a vacuum at  $100$ — $105^\circ$ . It forms large, colourless, oblique prisms, sometimes with a greenish lustre. They do not alter in dry air, but are decomposed by moisture with formation of hydrogen bromide and phosphorous acid. The latter at once reduces the gold to the metallic state.

*Auric phosphoric bromide*,  $\text{AuBr}_3, \text{PBr}_5$ , is obtained by heating the preceding compound with bromine in sealed tubes at  $120$ — $130^\circ$ . It crystallises from the excess of bromine, on cooling, in large deep-red crystals which may be dried in a vacuum at  $50^\circ$ . It can also be obtained by heating finely-divided gold with a solution of phosphoric bromide in bromine in sealed tubes at  $150^\circ$ .

When auric phosphoric bromide is heated at  $180^\circ$  with phosphorous bromide, phosphoric bromide and aurous phosphorous bromide are formed. Similarly, when finely-divided gold is heated with a solution of phosphoric bromide in phosphorous bromide, auric phosphoric bromide is formed, but its formation is limited by the tendency of the phosphorous bromide to reduce it to aurous phosphorous bromide. No such reducing action is observed with the corresponding chlorine compounds.

*Aurous phosphorous bromochloride*,  $\text{Au}_2\text{Br}_2, 2\text{PCl}_3$ , is obtained by heating aurous bromide with phosphorous chloride in presence of a small quantity of phosphorous bromide. It crystallises in colourless highly refractive oblique prisms, which do not alter in dry air, but are decomposed by moisture.

The formation of these double compounds affords additional proof of the definite existence of aurous bromide and chloride.

C. H. B.

**New Rhodium Compounds.** By C. VINCENT (*Compt. rend.*, **101**, 322—324).—When a warm concentrated solution of rhodium chloride is mixed with a warm concentrated solution of a methylammonium hydrochloride and the mixture cooled, the rhodium chloride and the hydrochloride of the amine combine to form crystalline double chlorides which separate more easily if the liquid contains an excess of the organic salt, when they are less soluble than in pure water.

*Monomethylammonium rhodiochloride*,  $(\text{NH}_3\text{MeCl})_8, \text{Rh}_2\text{Cl}_6$ , analogous to the hydrated chloride,  $\text{Rh}_2\text{Cl}_6 + 8\text{H}_2\text{O}$ , forms deep garnet-red anhydrous crystals which do not alter at  $140^\circ$ , and seem to belong to the rhombic system.

*Dimethylammonium rhodiochloride*,  $(\text{NH}_2\text{Me}_2\text{Cl})_6, \text{Rh}_2\text{Cl}_6 + 3\text{H}_2\text{O}$ , crystallises in deep garnet-red efflorescent prisms belonging to the rhombic system.

*Trimethylammonium rhodiochloride*,  $(\text{NMe}_3\text{Cl})_6, \text{Rh}_2\text{Cl}_6 + 9\text{H}_2\text{O}$ , forms long garnet-red prisms which are very soluble in water, and rapidly undergo alteration.

All three compounds melt when heated, and then decompose with intumescence, leaving a residue of metallic rhodium and charcoal; the latter readily burns away, and the pure metal is left.

Solutions of the rhodiochlorides give with silver nitrate a pinkish precipitate of silver rhodiochloride.

C. H. B.

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## Mineralogical Chemistry.

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**Native Tellurium from Fačzebaja.** By H. v. FOULLON (*Jahrb. f. Min.*, 1885, 1, Ref., 371—372).—The tellurium was found with quartz and iron pyrites in sandstone from the Dreifaltigkeit Adit Level, Fačzebaja. The largest of the groups of crystals attain dimensions of 3 to 4 mm. The character of the crystals is columnar, the rhombohedral planes being usually distorted. The author could find traces of the basal plane on two of the crystals only. The tellurium had the following composition:—

Tl.	Se.	Pyrites.	Quartz.	Total.
81.28	5.83	12.40	1.10	100.61

The tellurium crystals are free from gold, but rich in inclusions of pyrites.

B. H. B.

**Crystalline Form of Miargyrite.** By J. W. LEWIS (*Zeit. Kryst. Min.*, 8, 545—567; *Jahrb. f. Min.*, 1885, 1, Ref., 372—377).

**Limonite.** By J. C. WELCH (*Chem. News*, 52, 32—33).—This sample of mineral consisted of roundish particles, slightly flattened on two opposite sides, varying from  $\frac{1}{16}$  to  $\frac{1}{4}$  inch in diameter; these were imbedded in a ground-mass, apparently red sandstone. They were

brownish-red in colour, with an almost metallic lustre, and proved to be limonite of good composition, mixed with a considerable quantity of silica, amounting to 48 per cent. of the dry ore. The author attributes the variation in colour of various specimens of limonite to the silica present. According to this supposition the larger the proportion of silica the lighter the colour becomes, and *vice versâ*.

D. A. L.

**Priceite, Colemanite, and Pandermite.** By A. KENNGOTT (*Jahrb. f. Min.*, 1885, 1, Mem., 241).—The author shows, by recalculating the published analyses, that priceite, colemanite, and pandermite are varieties of the same mineral.

B. H. B.

**Pinnoite, a New Borate from Stassfurt.** By H. STAUTE (*Jahrb. f. Min.*, 1885, 1, Ref., 378—379).—The mineral described has been recently discovered, in association with boracite and kainite, in the salt deposit of Stassfurt. It is generally of a sulphur-yellow colour, but occasionally green. Under the microscope, crystalline faces may be detected, but the crystals are compressed together in such a manner that a determination of the crystalline form is impossible. From the behaviour of their sections between crossed Nicols, it is evident, however, that the crystals do not belong to the cubic system. The hardness of the mineral is 3 to 4, the sp. gr. 2·27. The analysis gave the following results:—

MgO.	B <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Fe.	Cl.
24·45	42·50	32·85	0·15	0·18

corresponding with the formula  $\text{MgB}_2\text{O}_4 + 3\text{H}_2\text{O}$ .

From the manner of its occurrence, the author concludes that pinnoite is a secondary product produced by the action of salt solutions on boracite.

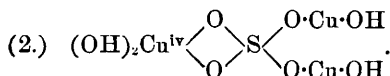
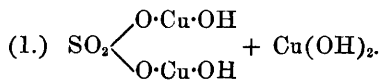
B. H. B.

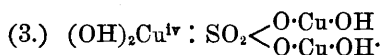
**Analysis of Artificial Brochantite.** By ATANASESCO (*Bull. Soc. Chim.*, 44, 14—16).—The samples of brochantite examined were prepared by heating copper sulphate and oxide in a sealed tube at 200°, also by heating copper sulphate and water in a similar manner.

The analyses of the different samples yielded practically identical results, agreeing with the composition—

H <sub>2</sub> O .....	10·15 per cent.
SO <sub>3</sub> .....	22·56 „
CuO .....	67·27 „

for which the author proposes the three following constitutional formulæ:—





The author finds that brochantite does not lose its water of constitution at  $150^\circ$  as formerly believed, and that it is only when exposed to the temperature of boiling mercury that it commences to lose weight, and then with great slowness.

In estimating the water of constitution in his analysis, the author employed the temperature of boiling sulphur. A. P.

**Diopside from Zermatt.** By A. STRENG (*Jahrb. f. Min.*, 1885, 1, Mem., 238—239).—In a specimen of vesuvian from Zermatt, a portion of the crystals was covered with calcite; and, in order to remove this, the author placed the specimen in dilute hydrochloric acid. By this means he detected small colourless tabular crystals planted on the vesuvian. The character of these crystals is peculiar. They form a combination of the forms:  $\infty P\infty$ ,  $0P$ ,  $\infty P$ ,  $\infty P3$ ,  $P$ ,  $2P$ ,  $3P$ ,  $-\frac{1}{2}P$ ,  $-P$ . As  $\infty P\infty$  predominates, the crystals appear tabular.  $P$ ,  $-P$ ,  $-\frac{1}{2}P$  are always subordinate. The axial ratio was calculated to be  $a:b:c = 1.09312:1:0.589456$ .  $\beta = 74^\circ 11\frac{1}{2}'$ . The crystals are colourless to white, with glassy lustre. The analysis gave the following results:—

SiO <sub>2</sub> .	CaO.	MgO.	FeO.	Ignition.	Total.	Sp. gr.
54.22	24.80	18.25	1.84	0.41	99.52	3.11

The mineral is, consequently, a colourless tabular diopside very poor in iron. B. H. B.

**Chloritoid from Morbihan.** By BARROIS (*Jahrb. f. Min.*, 1885, 1, Ref., 369—370).—In the schists of the Island of Groix, characterised by the occurrence of glaucophane (Abstr., 1884, 412), a mineral occurs resembling ottreolite in appearance, which the author, after a thorough investigation, regards as chloritoid. It occurs in greenish-blue plates, 1 to 10 mm. in diameter. The cleavage is perfect in one direction. It is not so perfect as that of mica, but more perfect than that of ottreolite. The cleaved plates are brittle. Horizontal dispersion is noticeable. The mineral is strongly dichroic. The analysis gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	H <sub>2</sub> O.	Total.
24.90	40.36	26.17	2.54	6.23	100.20

corresponding with the formula  $\text{H}_2\text{FeMgAl}_2\text{SiO}_7$ . A careful examination of plates cut perpendicular to the axes of elasticity showed the mineral to belong to the monoclinic system. B. H. B.

**Crystalline Form and Optical Characters of Sismondine.** By DES-CLOIZEAUX (*Jahrb. f. Min.*, 1885, 1, Ref., 370—371).—The author has examined the mineral resembling sismondine, which accompanies the glaucophane of the Val de Chisone in Piedmont and of Zermatt, and has compared it with the genuine sismondine from

San Marcello. The minerals have the same composition, an analysis of the Zermatt mineral giving the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	H <sub>2</sub> O.	Total.	Sp. gr.
24·40	42·80	19·17	6·17	6·90	99·44	3·32—3·40

The bisectrix is positive, not negative as was formerly believed. The dispersion of the optic axes is very considerable; the dispersion of the axes of elasticity is horizontal;  $\rho$  is greater than  $\nu$ .

The minerals that should be classed with sismondine, chloritoid, masonite, and phyllite, have the same optical properties as sismondine. The mineral described by Barrois (see preceding Abstract) more closely resembles sismondine than chloritoid. The large plates from the Silurian schists of the Ardennes, described by Renard and De la Vallée Poussin, with positive bisectrix and strong dichroism, do not belong to ottreolite, but to sismondine. Here, too,  $\rho$  is greater than  $\nu$ , the dispersion horizontal, and the optic axes form a large angle. The vénasquitte from Teulé (Finistère) forms a transition to ottreolite. It is strongly dichroic, and the bisectrix is positive, but the dispersion is weak. Ottreolite proper is but slightly dichroic and double refracting; the axial angle is variable, and  $\rho$  is less than  $\nu$  rather than  $\rho$  greater than  $\nu$ .  
B. H. B.

**Nephrite from Jordansmühl in Silesia.** By A. KENNGOTT (*Jahrb. f. Min.*, 1885, 1, Mem., 239—240).—The author has recalculated the analyses by H. Traube (Abstr., 1885, 361) of nephrite from Jordansmühl, and finds that the calculation does not give the formula RO, SiO<sub>2</sub> as stated. He is, therefore, of opinion that the mineral from Jordansmühl, although resembling nephrite, is not a true nephrite, as the percentage of silica is too high.  
B. H. B.

**Uranium Silicate from Garta.** By A. E. NORDENSKJÖLD (*Jahrb. f. Min.*, 1885, 1, Ref., 392).—The mineral described was found at Garta, near Arendal, in a mixture of orthoclase, calcite, fergusonite, clevéite, yttrio-gummite, zircon, quartz, and mica. It forms sulphur-yellow crystalline or radiated masses with double refraction. The hardness is less than 3, the sp. gr. 4·17. An analysis of 93 mgrams. gave the following results:—

SiO <sub>2</sub> .	U <sub>2</sub> O <sub>3</sub> .	CaO.	ThO <sub>2</sub> + YO.	PbO.	Ignition.	Total.
13·0	48·8	14·7	3·5	1·7	18·6	100·3

B. H. B.

**Origin of Manganese Minerals.** By DIEULAFIT (*Compt. rend.*, 101, 324—327).—The manganese minerals found in the district of Biot, Roquefort, and Villeneuve (Alpes Maritimes), in the pockets and hollows in the Oxford and coralline limestones, have been derived by the action of percolating water from the tertiary sandstones which lie above the limestones. These sandstones have themselves been derived from the denudation of primordial rocks, and contain a relatively large proportion of manganese, together with barium,

strontium, lithium, copper, and zinc. These latter metals can all be readily detected in the manganese minerals. Some parts of the sandstone are still rich in manganese, but other parts contain only very small quantities of this element, which has doubtless been removed by the percolating water.

C. H. B.

**Pyroxene-andesites from the Dutch Indian Archipelago.** By R. D. M. VERBEEK (*Jahrb. f. Min.*, 1885, 1, Mem., 243—244).—In the author's geological description of the west coast of Sumatra, published at Amsterdam in 1883, he mentions frequent pleochroic and non-pleochroic sections of augite in augite-andesites. The examination of pyroxene crystals from the Krakatoa ashes of 1883 led to the detection of brown pleochroic hypersthene and green non-pleochroic augites. Thin sections of this hypersthene coincide so perfectly with the pleochroic pyroxene sections of almost all the pyroxene-andesites of Sumatra and Java, that the sections must, without doubt, be regarded as hypersthene. In most of the andesites of the Dutch Indian Archipelago, hypersthene predominates over augite to such an extent that the name augite-andesite ought to be changed into hypersthene-andesite; or preferably the more general term, pyroxene-andesite, should be adopted.

B. H. B.

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## Organic Chemistry.

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**Condensation of Hydrocyanic Acid.** By O. v. D. PFORDTEN (*Ber.*, **18**, 1875—1878).—The author finds that when any acid is added to a solution of potassium cyanide in quantity insufficient to completely decompose the cyanide, the solution becomes yellow, then red, and finally dark claret-coloured. After a time, a dark brown precipitate is formed, the supernatant solution remaining of a claret colour. Free hydrocyanic acid added to a solution of pure potassium cyanide produces the same result. This reaction takes place more readily if the solution is heated on the water-bath. The author believes that the coloration is due to a condensation of hydrocyanic acid in the presence of potassium cyanide. It probably is the same coloration lately noticed by Habel (this vol., p. 233). L. T. T.

**Boiling Point Anomalies of the Chlorinated Acetonitriles and their Derivatives.** By H. BAUER (*Annalen*, **229**, 163—198).—*Dichloromethoxyacetonitrile*,  $\text{CCl}_2(\text{OMe})\cdot\text{CN}$ , obtained by the action of sodium methoxide on trichloroacetonitrile, boils at  $148-149^\circ$  (Bar. = 732 mm.); sp. gr. = 1.3885. It is readily soluble in alcohol, ether, and in hydrocarbons, but only sparingly in water, by which it is slowly decomposed with formation of hydrocyanic and hydrochloric acids. It polymerises when kept long. *Dichloromethoxyacetonitrile*,  $\text{CCl}_2(\text{OEt})\cdot\text{CN}$ , boils at  $160-161.5^\circ$ ; sp. gr. = 1.3394.



It is a strongly refractive liquid having an agreeable odour. *Dichloropropoxyacetonitrile*,  $\text{CCl}_2(\text{OPr})\cdot\text{CN}$ , boils between  $182$  and  $184^\circ$ ; sp. gr. =  $1.2382$  at  $15.5^\circ$ . It resembles the two compounds already described. *Dichloromonisobutoxyacetonitrile*,  $\text{CCl}_2(\text{OC}_4\text{H}_9)\cdot\text{CN}$ , is a colourless liquid which boils at  $195$ — $197^\circ$ ; sp. gr. =  $1.1226$  at  $15^\circ$ . *Monochlorodiethoxyacetonitrile*,  $\text{CCl}(\text{OEt})_2\cdot\text{CN}$ , was obtained by heating the monethoxy-derivative with sodium ethoxide at  $100^\circ$ ; it boils at  $159.5$ — $161.5^\circ$ . *Monochlorodipropoxyacetonitrile*,  $\text{CCl}(\text{OPr})_2\cdot\text{CN}$ , boils at  $199$ — $202^\circ$ . *Triethoxyacetonitrile*,  $\text{C}(\text{OEt})_3\cdot\text{CN}$ , boils at  $159$ — $161.5^\circ$ ; sp. gr. =  $1.0030$ . *Tripropoxyacetonitrile*,  $\text{C}(\text{OPr})_3\cdot\text{CN}$ , boils at  $216$ — $219^\circ$ . *Monochloropropethoxyacetonitrile*,  $\text{PrO}\cdot\text{CCl}(\text{OEt})\cdot\text{CN}$ , boils at  $182$ — $184^\circ$ , that is, at a temperature half way between the boiling point of the diethoxyl and that of the dipropoxyl compound.

The *platinochlorides* of dichloromethoxy-, dichlorethoxy-, and dichloropropoxy-acetonitriles were prepared; they are red powders, which decompose in the presence of water. When the monalkoxyl-derivatives are treated with hydrochloric acid, they yield trichloroacetamide. Dilute sulphuric acid acts on them with formation of methyl (or ethyl) trichloroacetate. When dichlorisobutylacetonitrile is heated with gaseous hydrogen chloride, it yields isobutyl chloride and trichloroacetamide.

According to Kopp (*Annalen*, **96**, 16), the substitution of methoxyl for chlorine has, in many cases, no influence on the boiling point; on the other hand, chlorine is sometimes, as in the case of the compounds described here, equivalent to ethoxyl; for when one atom of chlorine (in trichloroacetonitrile) is substituted for ethoxyl, the substitution of the second and third atoms of chlorine does not affect the boiling point. N. H. M.

**Action of Phosphonium Iodide on Ethylene Oxide.** By J. DE GIRARD (*Compt. rend.*, **101**, 478—479).—Phosphonium iodide reacts very energetically with ethylene oxide, with formation of hydrogen phosphide, hydrogen iodide, and ethylene di-iodide melting at  $81$ — $82^\circ$ . Ethylene oxide therefore differs very considerably from its isomeride aldehyde in its behaviour towards phosphonium iodide, and resembles ether, ethyl alcohol, and propyl alcohol, which all yield the corresponding iodides when brought in contact with phosphonium iodide in the cold. In other words, phosphonium iodide acts towards these bodies and ethylene oxide simply as a source of hydrogen iodide. C. H. B.

**Physical Properties of Chloroacetates.** By L. HENRY (*Compt. rend.*, **101**, 250—253).—The substitution of chlorine for hydrogen in the  $\text{CH}_3$  group in acetic derivatives produces a progressive increase in the molecular weight and a diminution in the proportion of hydrogen, and these changes are accompanied by changes in the physical properties of the compounds, more especially in their volatility and sp. gr. In the chloroacetic acids and methyl chloroacetates, the substitution of chlorine for hydrogen causes a progressive rise in the boiling point and increase in the sp. gr., but in neither case is the difference constant. The effect produced by the

substitution of the first atom of chlorine is much greater than that which follows the substitution of the two other atoms.

	B. p.	Diff.	Sp. gr. at 19.2°.	Diff.
$\text{CH}_3\cdot\text{COOMe}$ ....	55°		0.9238	
$\text{CH}_2\text{Cl}\cdot\text{COOMe}$ ..	130	+ 75	1.2352	0.3114
$\text{CHCl}_2\cdot\text{COOMe}$ ..	144	+ 14	1.3808	0.1456
$\text{CCl}_3\cdot\text{COOMe}$ ....	154	+ 10	1.4892	0.1084

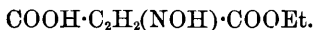
The substitution of Cl for H in acetic acid with formation of monochloroacetic acid, and in dichloroacetic acid forming the trichlorinated derivative, produces an increase of 46° in the melting point, but the melting point of dichloroacetic acid is 50° lower than that of the monochlorinated derivative. The replacement of  $\text{H}_2$  by  $\text{Cl}_2$  in either acetic or monochloroacetic acid produces a reduction of 4° in the melting point. Precisely similar relations are observed in the chloracetamides. Dichloroacetamide is also characterised by an anomalous solubility.

It is important to observe that all acetic derivatives are *odd* or *even* substitution-derivatives of methane, and Regnaud and Villejean have already shown that the odd or even chlorinated derivatives of methane differ considerably in their physiological properties (this vol., p. 926).

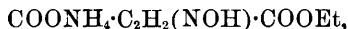
C. H. B.

**Constitution of Ethyl Succinosuccinate.** By H. EBERT (*Annalen*, 229, 45—88).—*Dimethylic succinosuccinate*,  $\text{C}_{10}\text{H}_{12}\text{O}_6$ , closely resembles the ethyl salt; it is fluorescent, and melts at 152°.

*Ethylic dinitrososuccinosuccinate*,  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_8$ , obtained by acting on ethyl succinosuccinate with nitrous acid in ethereal solution, forms a fine white powder which becomes brown on exposure to air. It is insoluble in the usual solvents. When heated it becomes brown at 100°, and melts with decomposition and evolution of gas at 113—114°. It gives the nitroso-reaction with phenol and sulphuric acid. When treated with anhydrous alcohol, the ethylic salt of quinone dihydride-dicarboxylic acid, a compound already prepared by Hermann (*Abstr.*, 1883, 1084), is formed, and gases containing nitric oxide are evolved. When heated with water, ethyl  $\alpha$ -oximidopropionate (Meyer and Züblin, *Abstr.*, 1878, 659) is formed with evolution of carbonic anhydride; cold water, on the other hand, acts without evolution of carbonic anhydride, and yields *monethyl oximidosuccinate*,



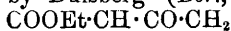
The latter compound is soluble in water, alcohol, and hot chloroform, sparingly soluble in benzene; it becomes brown on exposure to air, and melts with decomposition at 110—111°. It does not give Liebermann's nitroso-reaction; it reacts strongly acid with litmus and decomposes carbonates. The *ammonium salt*,



and the corresponding *sodium*, *magnesium*, *calcium* (with 2 mols.  $\text{H}_2\text{O}$ ), *barium*, *silver*, and *zinc* salts, were prepared. Some of these salts when heated give a sublimate of ethyl  $\alpha$ -oximidopropionate. When

an aqueous solution of the monethyl salt is treated with twice the quantity of lime necessary for the formation of the above-mentioned calcium salt, the whole of the lime dissolves and a *calcium salt*,  $C_6H_7CaNO_5 + 2H_2O$ , is obtained; the corresponding *barium salt*, with 1 mol.  $H_2O$ , is described. By acting on ethyl oximidosuccinate with sodium ethoxide, and subsequent treatment with silver nitrate, a *silver salt*,  $C_4H_3Ag_2NO_5$ , was obtained, which yielded free *oximidosuccinic acid*,  $COOH \cdot C_2H_2(NO \cdot H) \cdot COOH$ . This dissolves readily in alcohol and water, but only sparingly in ether, and is practically insoluble in benzene, chloroform, and light petroleum. It decomposes at  $126^\circ$ . When neutralised with ammonia, it gives a green precipitate with copper acetate, and a brown precipitate with ferric chloride. The *calcium salt*,  $C_4H_3CaNO_5 + 4H_2O$ , is described. The *diethyl salt*,  $COOEt \cdot C_2H_2(NO \cdot H) \cdot COOEt$ , has no action on carbonates, but is soluble in baryta-water and in potash. The formation of these salts, and the fact that the monethyl salt is easily changed to ethyl  $\alpha$ -nitrosopropionate, can only be accounted for by the constitutional formula ascribed to it.

The largeness of the yield of monethyl amidosuccinate obtained from ethyl dinitrososuccinosuccinate shows that 1 mol. of the latter compound decomposes with formation of 2 mols. of ethyl oximidosuccinate. This proves, indirectly, the correctness of the constitution ascribed by Duisberg (*Ber.*, **16**, 137) to ethyl succinosuccinate,

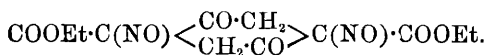


namely:  $\begin{array}{c} | \qquad \qquad | \\ CH_2 \cdot CO \cdot CH \cdot COOEt \end{array}$  (Compare also *Abstr.*, 1883,

1084.) A substitution product of a compound, of the constitution  $CH_2 \cdot CO \cdot CH \cdot COOEt$

$\begin{array}{c} | \qquad \qquad | \\ CH_2 \cdot CO \cdot CH \cdot COOEt \end{array}$ , that originally proposed by Hermann (*Abstr.*,

1882, 712) would give, not 2 mols. of a monethyl salt, but 1 mol. of a free acid and 1 mol. of a diethyl salt. The constitution of ethyl dinitrososuccinosuccinate would then be



N. H. M.

**Derivatives of Levulinic Acid.** By L. WOLFF (*Annalen*, **229**, 249—285).—Levulinic acid is partially decomposed by slow distillation, the distillate consisting of a mixture of water, unaltered levulinic acid, and  $\alpha$ - and  $\beta$ -angelica lactones. The relative quantities of the two lactones produced vary with the rate of distillation. The oily portion of the distillate is treated with potassium carbonate, washed with water, and separated by fractional distillation into two portions boiling at  $165$ — $170^\circ$  and  $200$ — $210^\circ$  respectively.

$\alpha$ -Angelica lactone,  $C_5H_6O_2$ , is a colourless liquid boiling at  $167^\circ$ . At  $0^\circ$  it solidifies, forming six-sided prisms or needles, which melt at  $18^\circ$  and dissolve freely in the usual solvents.

The  $\beta$ -lactone is obtained when the distillation of the levulinic acid is carried on more rapidly than in the preparation of the  $\alpha$ -lactone. Less than two hours are required for the distillation of 30 grams of

acid. The mixture of lactones in the distillate is purified by treatment with potassium carbonate and washing with water. It is then distilled under a pressure of 25 mm. Under these circumstances, the  $\alpha$ -lactone boils at  $51^\circ$ , and the  $\beta$ -lactone at  $83^\circ$ . The fraction boiling between  $72^\circ$  and  $90^\circ$  is boiled with water for four hours in a flask provided with a reflux condenser. The  $\alpha$ -lactone is quantitatively converted into levulinic acid, but as the  $\beta$ -lactone is more stable, the greater portion of it remains unaltered.  $\beta$ -Angelica lactone is a colourless liquid which does not solidify at  $-17^\circ$ . It is miscible with water in all proportions. The sp. gr. at  $0^\circ$  is 1.1084. Under a pressure of 751 mm. it boils at  $208^\circ$  with partial conversion into the  $\alpha$ -lactone. The  $\alpha$ -lactone is converted quantitatively into barium levulinate by treatment with baryta-water; the  $\beta$ -lactone also yields the same salt.

Ammonia converts  $\alpha$ -angelica lactone into the amide of levulinic acid,  $C_5H_7O_2 \cdot NH_2$ . This compound is deposited from warm chloroform in six-sided plates melting at  $107^\circ$ . It dissolves freely in water and alcohol, and is decomposed by acids and alkalis into levulinic acid and ammonia.

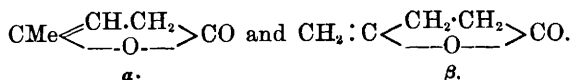
A solution of bromine in carbon bisulphide acts energetically on  $\alpha$ -angelica lactone, converting it into *dibromovalerolactone*, a crystalline hygroscopic compound melting at  $81^\circ$ ; this is decomposed by water, yielding monobromolevulinic acid,  $C_5H_7O_3Br$ . The acid melts at  $59^\circ$ ; it is soluble in water, alcohol, and ether.

$\beta$ -Angelica lactone also unites with bromine, forming a non-crystallisable syrup, which is decomposed by water, yielding monobromolevulinic acid.

The  $\alpha$ -lactone unites with hydrogen chloride, forming monochlorovalerolactone,  $C_5H_7O_2Cl$ . This substance readily absorbs moisture from the atmosphere, and decomposes into hydrochloric and levulinic acids. It is decomposed by distillation under the ordinary atmospheric pressure, hydrogen chloride being evolved, and  $\beta$ -angelica lactone produced. Monochlorovalerolactone is attacked by bromine, yielding a dibromo-substitution product. This substance is a thick non-crystallisable syrup; it is decomposed by water, forming monobromo- and dibromo-levulinic acids.

Concentrated hydrochloric or hydrobromic acid dissolves the  $\alpha$ -lactone, and on the addition of water, levulinic acid is produced. A small quantity of hydrochloric acid is capable of transforming a considerable quantity of the lactone into levulinic acid if sufficient water is present. The  $\beta$ -lactone is not acted on by hydrochloric acid.  $\alpha$ -Angelica lactone is not affected by nascent hydrogen.

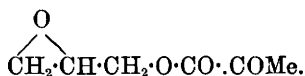
The lactones are not the sole products of the destructive distillation of levulinic acid. Small quantities of acetic acid and of a crystalline acid of the composition  $C_{10}H_{10}O_3$  are also formed. The constitution of the isomeric angelica lactones may be represented by the following formulæ:—



W. C. W.

**Decomposition of Tartaric Acid in the Presence of Glycerol.**

By K. JOWANOWITSCH (*Monatsh. Chem.*, **6**, 467—476).—When a mixture of 8 parts tartaric acid and 10 parts glycerol is heated at 140°, large quantities of carbonic anhydride are evolved; at 180° a small quantity of acraldehyde is given off, and at a still higher temperature, 200—260°, a distillate is obtained containing pyruvic acid, acraldehyde, glycerol, and a crystalline substance, *glycidic pyruvate*,



The latter dissolves very readily in water, alcohol, and benzene, &c.; it melts at 78° (uncorr.). When boiled with calcium carbonate, it yields glycerol, pyruvic acid, and carbonic anhydride; it is converted into lactic acid by the action of reducing agents.

The author intends continuing the examination of the substance.

N. H. M.

**Synthesis of a New Tetrabasic Acid and an Isomeride of Aconitic Acid.** By G. SCHACHERL (*Annalen*, **229**, 89—101).—By the action of ethylic sodiomalonate on ethyl bromomaleate, a compound, *ethyl propargylenetetracarboxylate*,  $\text{C}_7\text{H}_2\text{O}_8\text{Et}_4$ , is obtained; it is a pale yellow liquid heavier than water. When treated with alcoholic soda, it yields a sodium salt, from which an acid—*propargylenetetracarboxylic acid*,  $\text{C}_7\text{H}_2\text{O}_8 + 2\text{H}_2\text{O}$ , may be obtained. The acid gives up its water of crystallisation at 100°. The *sodium salt* crystallises in small prisms with 8 mols.  $\text{H}_2\text{O}$ . The *barium salt* (with  $1\frac{1}{2}$  mol.  $\text{H}_2\text{O}$ ) and *calcium salt* (with  $3\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ ), are also described.

When propargylenetetracarboxylic acid is distilled, it gives off carbonic anhydride, and yields *pseudaconitic acid*,  $\text{C}_6\text{H}_6\text{O}_6$ , melting at 186—187°. A *barium salt*,  $(\text{C}_6\text{H}_3\text{O}_6)_2\text{Ba}_2 + \text{H}_2\text{O}$ , was prepared.

N. H. M.

**Monobromo- and Dibromo-pyromucic Acid.** By H. B. HILL (*Gazzetta*, **15**, 111).—A controversial note in reference to Canzoneri and Oliveri's paper (this vol., p. 244).

**Monobromo- and Dibromo-pyromucic Acid.** By F. CANZONERI and V. OLIVERI (*Gazzetta*, **15**, 111).—An answer to the above.

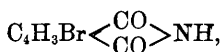
**Oxidation of Carbon by the Electrolysis of a Solution of Ammonia.** By A. MILLOT (*Compt. rend.*, **101**, 432—433).—The author has already stated (Abstr., 1880, 482, and 1883, 65) that when a solution of ammonia is electrolysed with a positive electrode of purified gas-carbon and a negative electrode of platinum, the liquid acquires a deep black colour. If this black solution is evaporated to dryness on a water-bath, and the residue exhausted with warm alcohol, a black insoluble substance is left, and a yellow solution is obtained. When this solution is evaporated to a syrup, it deposits a yellowish nitrogenous substance, soluble in boiling water, to which it imparts an acid reaction. The still liquid portion is evaporated repeatedly until no further deposit is obtained, and when the filtered

liquid is allowed to cool it deposits crystals of carbamide. The non-crystallisable acid substance has not, as stated by Bartoli and Papisogli, the properties of mellitic acid or its derivatives.

When the black substance insoluble in alcohol is oxidised by sodium hypochlorite, it yields a nitrogenous substance, soluble in boiling water (*loc. cit.*), but no mellitic acid is formed.

In this reaction the synthesis of carbamide is effected by the direct action of carbonic anhydride and ammonia under the influence of the electric current. The electrolysis during eight days of 500 c.c. of ammonia mixed with an equal volume of water gave 6—8 grams of the black substance and 1 gram of pure carbamide. C. H. B.

**Monobromo- and Dibromo-citraconimide.** By D. MENDINI (*Gazzetta*, 15, 182—185).—*Monobromocitraconimide*,



prepared by the action of bromine on pyrotartarimide or citraconimide, crystallises in needles or leaflets melting at 179—182°, of slightly acid reaction, insoluble in cold, moderately soluble in hot water, soluble in boiling alcohol; it forms a silver-derivative.

*Dibromocitraconimide*,  $\text{C}_4\text{H}_2\text{Br}_2 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{NH}$ , prepared in a manner similar to the above compound, crystallises in iridescent leaflets melting at 142—144°, soluble in alcohol, and more soluble in water than the monobromo-derivative. V. H. V.

**Constitution of Thiophen.** By J. THOMSEN (*Ber.*, 18, 1832—1833).—The author is led to consider from his researches on the heat of formation of thiophen that the four carbon-atoms are united by five single bonds, and that it is probable that like benzene it will yield three bisubstitution-compounds. A. P.

**Paraxylene in Galician Petroleum.** By B. PAWLEWSKI (*Ber.*, 18, 1915—1916).—In a petroleum from Kleczany, West Galicia, the author obtained about 2 per cent. of aromatic hydrocarbons, which consisted principally of benzene and paraxylene. Paraxylene has not hitherto been detected in Galician petroleum. L. T. T.

**Benzene Hexabromide.** By J. MEUNIER (*Compt. rend.*, 101, 378—381).—Bromine is allowed to fall drop by drop into benzene boiling in direct sunlight, and after excess of bromine has been added the boiling is continued for some time. As the liquid cools, benzene hexabromide crystallises out, and is separated from the liquid products, washed with an alkaline solution, pressed, dried, and carefully sublimed. The first portion of the sublimate, which consists mainly of tribromobenzene, is rejected, and the perfectly white crystalline flakes or lamellæ which subsequently sublime are dissolved in a boiling mixture of benzene and alcohol, and allowed to crystallise slowly. Benzene hexabromide crystallises in large oblique rhombic prisms, which are strictly isomorphous with those of the  $\alpha$ -hexachloride.

Measurements of the inclinations of the axes and faces are given in the original paper.

The liquid products formed in the preparation of the hexabromide consist mainly of monobromobenzene, which is obtained in very much larger quantity than the hexabromide, together with some tribromobenzene. In the preparation of the hexachloride under similar conditions, only a very small proportion of monochlorobenzene is obtained.

C. H. B.

**Benzene-derivatives obtained by the Action of Carbonic Oxide on Potassium.** By R. NIETZKI and T. BENCKISER (*Ber.*, **18**, 1833, 1843. Compare this vol., p. 779).—The authors consider the compound  $C_6K_4O_6$ , obtained by the action of carbonic oxide on potassium, to be the potassium-derivative of hexahydroxybenzene; the freshly-prepared substance is not explosive, but becomes so on keeping. On treating it first with strong and subsequently with dilute alcohol, the potassium salt of the dihydroxycarboxylic acid of Lerch (*Annalen*, **124**, 20) is obtained. The authors consider this to be the potassium-derivative of tetrahydroxyquinone,  $C_6(OK)_4O_2$ ; the free quinone may be obtained by treating it with dilute acids. If the free quinone is treated with sodium carbonate in the presence of air, a disodium-derivative,  $C_6(ONa)_2(OH)_2O_2$ , is formed. Rhodizonic acid, the authors regard as being dihydroxydiquinoyl,  $C_6(OH)_2(O_2)_2$ .

A. P.

**Preparation of Nitro-derivatives of Aromatic Amines.** By I. LEVINSTEIN (*Dingl. polyt. J.*, **256**, 471).—On treating the nitrates of aromatic amines with cold concentrated sulphuric acid, nitro-derivatives are obtained, and it appears that metanitro-compounds are almost exclusively produced. Aniline gives a product melting at  $107^\circ$ ; its acetyl derivative has a melting point of  $143^\circ$ , and on reduction a phenylenediamine is obtained, which yields Bismark brown when treated with nitrous acid. Orthotoluidine gives a nitrotoluidine melting at  $106^\circ$ , and crystallising in long needles from alcohol and in thick prisms from toluidine (? toluene). Its constitution is probably  $[Me:NH_2:NO_2 = 1:2:4]$ . It yields a toluylenediamine on reduction, which forms brown colouring matters when treated with nitrous acid. When paratoluidine is treated as above, an orthonitrotoluidine is obtained, which melts at  $77-78^\circ$ , and has the constitution  $[Me:NO_2:NH_2 = 1:2:4]$ . On reduction, metatoluylenediamine is obtained.

D. B.

**Action of Reducing Agents on Nitrotoluidines.** By F. GRAEFF (*Annalen*, **229**, 340—352).—*Hydrazoaniline* has been investigated by Haarhaus (*Annalen*, **135**, 162), Buckney (*Abstr.*, 1878, 863), and Gilbert. It is best prepared by the reduction of metanitrilaniline with zinc-dust and alcoholic potash.

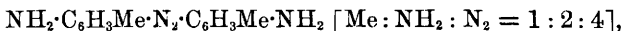
The action of sodium amalgam and of zinc-dust in presence of alcoholic potash on the nitrotoluidines gave the following results:  $C_6H_3Me(NO_2) \cdot NH_2$   $[1:3:4]$ , melting at  $114^\circ$ , is converted into toluylenediamine, melting at  $88.5^\circ$ . The nitrotoluidines,

$[Me:NO_2:NH_2 = 1:2:3 \text{ and } 1:3:2]$ ,

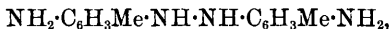
merely yield resinous products, but the 1:4:2 compound yields *azoxytoluidine*,  $(C_6H_3Me \cdot NH_2)_2N_2O$ . This crystallises in silky needles, soluble in alcohol and ether. It melts at  $168^\circ$ , and unites with acids to form crystalline salts. The *sulphate*,  $C_{14}H_{16}N_4O \cdot H_2SO_4 + \frac{1}{2}H_2O$ , is sparingly soluble in alcohol and ether. The *hydrochloride*,  $C_{14}H_{16}N_4O \cdot 2HCl$ , is soluble in water and in weak alcohol. The *platinochloride* forms microscopic needle-shaped crystals. The *nitrate* forms pale yellow plates. It is precipitated from aqueous solutions by the addition of ether or alcohol.

Strong sulphuric acid converts azoxytoluidine into *hydroxyazotoluidine*,  $NH_2 \cdot C_6H_3Me(OH) \cdot N_2 \cdot C_6H_3Me \cdot NH_2$ , which crystallises in dark-red needles. The base dissolves freely in alcohol and ether. It melts at  $212^\circ$  with decomposition. It unites with acids forming crystalline salts; the *sulphate*,  $C_{14}H_{16}N_4O \cdot H_2SO_4$ , is sparingly soluble in alcohol and water. The *hydrochloride* forms reddish-yellow prisms, soluble in water. The *platinochloride* dissolves in hot water, and is deposited from the solution in dark-red needles. It is decomposed by the action of stannous chloride, yielding toluylenediamine,  $C_6H_3Me(NH_2)_2$  [1:2:4], and diamidocresol,  $C_6H_2Me(NH_2)_2 \cdot OH$ .

An alcoholic solution of azoxytoluidine is reduced to azotoluidine by the action of sodium amalgam. Azotoluidine,



crystallises in large red needles, and also in smaller yellow needles. Both varieties melt at  $197^\circ$ , and dissolve freely in alcohol and ether. The *sulphate* and *hydrobromide* crystallise in red needles, which dissolve in water, but are insoluble in alcohol and ether. The *hydrochloride* forms pale-red plates, insoluble in alcohol and ether. The *platinochloride* is insoluble in alcohol and ether; sparingly soluble in water. When azotoluidine in alcoholic solution is treated with sodium amalgam, it is reduced to *hydrazotoluidine*,



a crystalline base, soluble in water and in weak alcohol. The *sulphate*,  $C_{14}H_{16}N_4 \cdot H_2SO_4$ , *hydrochloride*, and *hydrobromide*, which crystallise in needles, and the *platinochloride*, which forms rhombic prisms, are soluble in water, but insoluble in ether or absolute alcohol.

On reduction with stannous chloride or zinc-dust and potash, hydrazotoluidine is converted into a tolulenediamine, melting at  $99^\circ$ .

W. C. W.

**Pentamethylaniline.** By A. W. HOFMANN (*Ber.*, 18, 1821—1828). —*Pentamethylaniline*,  $C_6Me_5 \cdot NH_2$  (Abstr., 1883, 324), may be prepared by heating dimethylcumidine hydriodide in a sealed tube at  $240$ — $250^\circ$  for eight hours. It crystallises in large colourless needles which float on water; it melts at  $151$ — $152^\circ$ , and boils without decomposition at  $277$ — $278^\circ$ . It is insoluble in water, but dissolves readily in alcohol or ether. The *hydrochloride*,  $C_6Me_5 \cdot NH_2 \cdot HCl$ , forms long branched needles, soluble in hot, but not in cold water. The *platinochloride*,  $(C_6Me_5 \cdot NH_2)_2 \cdot H_2PtCl_6$ , forms rhombic plates, sparingly soluble in water. The *nitrate*, *sulphate*, *oxalate*, and *acetate* were also



prepared. The free base does not yield any colour reaction when heated with mercurous chloride. If, however, a small quantity of aniline is present, a colour analogous to rosaniline is formed. The *acetyl compound* of pentamethylaniline is readily obtained by treating the base with acetic anhydride. It melts at  $213^{\circ}$ .

*Pentamethylmethylaniline*,  $C_6Me_5 \cdot NHMe$ , is readily obtained by heating pentamethylaniline with methyl iodide in a sealed tube at  $100^{\circ}$ . It crystallises from alcohol in scales, and melts at  $60-61^{\circ}$ ; the *platinochloride*,  $(C_6Me_5 \cdot NHMe)_2, H_2PtCl_6$ , was prepared.

*Pentamethyldimethylaniline*,  $C_6Me_5 \cdot NMe_2$ , may be prepared by digesting pentamethylaniline with an alkali and methyl iodide; it is very similar to the methylaniline compound, and melts at  $53-54^{\circ}$ ; the *platinochloride*,  $(C_6Me_5 \cdot NMe_2)_2, H_2PtCl_6$ , was also prepared. Attempts to insert a further methyl molecule into this compound were unsuccessful.

*Pentamethylbenzonitrile*,  $C_6Me_5 \cdot NC$ , may be obtained by heating a solution of pentamethylaniline in alcoholic soda with chloroform. It forms colourless crystals, melts at  $127-128^{\circ}$ , and has the characteristic odour of the isonitriles.

*Pentamethylbenzonitrile*,  $C_6Me_5 \cdot CN$ , obtained by heating the isocompound a little above its melting point, is soluble in ether and alcohol, but insoluble in water; it forms colourless needles, melts at  $168^{\circ}$ , and boils at  $290-292^{\circ}$ ; it is a very stable compound, and is not acted on by sulphuric acid at  $100^{\circ}$  or by heating under pressure at  $180^{\circ}$  with concentrated hydrochloric acid, but it becomes carbonised on raising the temperature to  $230-250^{\circ}$ . By heating with concentrated hydriodic acid for some hours at  $220-230^{\circ}$ , ammonia and a crystalline hydrocarbon melting at  $52-53^{\circ}$  are formed; this compound was not further investigated, but is probably the pentamethylbenzene obtained by Friedel and Crafts (*Ann. Chim. Phys.* [6], 1, 472). Several attempts were made to obtain the amide from the nitrile, but without success.

*Pentamethylphenol*,  $C_6Me_5 \cdot OH$ , is obtained by treating pentamethylaniline sulphate with sodium nitrite and sulphuric acid; it forms slender colourless needles, has a phenolic odour, melts at  $125^{\circ}$  and boils at  $267^{\circ}$ ; the yield is about 70 per cent. of the theoretical; it gives no coloration with ferric chloride; it does not combine very readily with alkalis, and is difficult to burn; its combustion must be made in oxygen. The *methyl ether* of pentamethylphenol,  $C_6Me_5 \cdot OMe$ , is obtained by digesting a solution of the phenol in methyl alcohol with potash in a sealed tube at  $120^{\circ}$ ; it forms long slender needles and melts at  $63-64^{\circ}$ .

*Pentamethylbenzenethiocarbimide*,  $C_6Me_5 \cdot NCS$ , is obtained by heating pentamethylaniline with carbon bisulphide for several days, until only traces of sulphuretted hydrogen are given off; the thiocarbimide is separated by distillation from the ethereal carbamide formed at the same time, and is obtained in needles having an odour of oil of mustard; it melts at  $86^{\circ}$ . By digesting with alcoholic ammonia, *monopentamethylbenzenethiocarbamide*,  $NH_2 \cdot CS \cdot NH \cdot C_6Me_5$ , is formed; it may be crystallised from alcohol in needles and melts at  $224^{\circ}$ .

*Dipentamethylbenzenethiocarbamide*,  $C_6Me_5 \cdot NH \cdot CS \cdot NH \cdot C_6Me_5$ , which

is formed along with the pentamethylbenzenethiocarbamide, is sparingly soluble in alcohol, but may be crystallised from glacial acetic acid in the form of colourless needles. It melts at  $252^{\circ}$ .

A. P.

**Derivatives of Thiodiphenylamine.** By N. FRAENKEL (*Ber.*, **18**, 1843—1849).—Thiodiphenylamine prepared by the method given by Bernthsen (*Abstr.*, 1884, 597) is a neutral substance, and does not combine with hydrochloric acid; when heated with zinc-dust or zinc chloride, it is partly reconverted into diphenylamine.

*Benzoylthiodiphenylamine*,  $C_{12}H_9NS\dot{B}z$ , prepared by heating thiodiphenylamine, benzoic chloride, and light petroleum for four hours in a sealed tube at  $100^{\circ}$ , forms colourless silky crystals; it is readily soluble in the usual solvents, and melts at  $170.5^{\circ}$ ; on heating to a higher temperature it is decomposed, sulphuretted hydrogen being formed. It is acted on by nitric acid in a manner similar to the acetyl derivative; the nitro-derivative formed yields Lauth's blue on adding first stannous chloride and then ferric chloride; cold concentrated sulphuric acid dissolves the benzoyl compound, forming a yellow solution, which becomes violet on heating.

*Ethyl thiodiphenylcarbamate*,  $SC_{12}H_9N\cdot COOEt$ , prepared by heating together thiodiphenylamine, ethyl chlorocarbonate, and ethyl ether in a sealed tube at  $100^{\circ}$ , and subsequently at  $120^{\circ}$ , for eight hours, forms white silky crystals, which melt at  $109\text{--}110^{\circ}$ , and may be distilled unaltered. It is readily soluble in the usual solvents, and on heating with alcoholic potash is saponified, thiodiphenylamine being reformed. It is soluble without colour in concentrated sulphuric acid, but on heating the colour characteristic of thiodiphenylamine is developed; ethyl thiodiphenylcarbamate is soluble in cold fuming nitric acid, but is precipitated unaltered on the addition of water; on heating with the acid, however, it is nitrated, and yields Lauth's colour reaction.

*Thiodiphenylcarbamic chloride*,  $C_{12}H_9SN\cdot COCl$ , prepared by heating diphenylamine with excess of a solution of carbonyl chloride in toluene for eight hours at  $100^{\circ}$  in a sealed tube, forms tufts of thick colourless needles or prisms, which melt at  $167.5^{\circ}$ , forming a green liquid; it is soluble in the usual solvents, and is quite unacted on in the cold by either fuming nitric acid or a mixture of this with sulphuric acid. Like Michler's diphenylcarbamic chloride (*Ber.*, **9**, 711) thiodiphenylcarbamic chloride when heated with aniline at  $180^{\circ}$  forms carbanilide and thiodiphenylamine.

*Dithiotetraphenylcarbamide*,  $CO(NC_{12}H_9S)_2$ , may be obtained by heating equal quantities of thiodiphenylcarbamic chloride and thiodiphenylamine with benzene in a sealed tube at  $200^{\circ}$  for four hours. It forms almost colourless scales, similar in appearance to thiodiphenylamine; it melts at  $223\text{--}225^{\circ}$ . It is very slightly soluble in alcohol, but readily in most other solvents; it dissolves in hot fuming nitric acid, but is deposited unaltered on adding water.

A. P.

**Formation of Rosaniline by the Nitrobenzene Process.** By M. LANGE (*Ber.*, **18**, 1918—1920).—It is generally supposed that in the above process the nitro-derivative gives up its oxygen, becomes

reduced to the corresponding amine, and that this then enters directly into the formation of the rosaniline molecule.

The author finds that it is immaterial whether nitrobenzene, nitrochlorobenzene, nitraniline, dinitrobenzene, or nitronaphthalene is employed as the oxidising agent. The resulting product is always the same, as the nitro-derivative acts merely as an oxidiser, and does not take part directly in the formation of the rosaniline molecule.

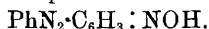
With methylated nitro-derivatives, the reaction is more complicated, but here also the nitro-compound does not enter into the reaction as a whole, and it is immaterial whether nitrotoluene, nitro-xylene, or nitromesitylene is employed: in these reactions, the nitro-compound not only gives up oxygen, but also its alkyl radicles. Thus a pure aniline, which when oxidised with nitrobenzene in the presence of ferric chloride gave only induline, yielded a melt containing a considerable quantity of magenta, when the nitrobenzene was replaced by paranitrotoluene. That this formation was not due to the direct action of the nitrotoluene was proved by replacing the latter by paranitrotoluenesulphonic acid, when magenta was again obtained, and not a trace of a sulphonic derivative. Similar results were obtained with orthonitrotoluene, dinitro-xylene, and trinitromesitylene; with the last two there was an evolution of methyl chloride. L. T. T.

**Products of the Reduction of Nitrazo-compounds: Nitrolic Acids.** By J. JANOVSKY (*Monatsh. Chem.*, **6**, 455—466).—This is in part repetition of a paper by Janovsky and Erb (this vol., p. 894).

*Dimetadiamidoazobenzene*,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4)_2\text{N}_2$ , is obtained by reducing the dinitro-derivative; it crystallises from alcohol in small yellow needles; its solution in hydrochloric acid has a splendid red colour. When treated with ferric chloride, it gives a red colour which becomes brown on being heated. It dyes wool and silk a fine yellow colour. Various salts are described.

*Diparadiamidoazobenzene* obtained from paradinitrazobenzene, crystallises from alcohol in microscopic plates, which melt at  $142^\circ$ . When treated with chromic mixture, it acquires an intense wine-red colour, and quinone is formed; it also gives a red colour with ferric chloride.

The behaviour of the nitrolic acids obtained by reducing di- and trinitrazobenzenes shows that the  $\text{—N} \cdot \text{OH}$  group contained in them is joined to two adjacent carbon-atoms in the benzene-ring; thus, for example, the constitution of paranitrolic acid would be



The analyses also agree better with these formulæ, which contain one atom of hydrogen less than those previously given (*loc. cit.*). The nitrolic acids, when heated, evolve nitric oxide; they reduce silver solutions, and are decomposed by long boiling with potassium hydroxide. When reduced in acid solution, they yield amido-derivatives of benzene.

*Triamidoazobenzene* was obtained from asymmetrical trinitrazobenzene; its hydrochloride is described. N. H. M.

**Constitution of Phenylazothymol.** By G. MAZZARA (*Gazzetta*, **15**, 228—232).—In order to determine the constitution of phenyl- and

diphenyl-azothymol, recently described by the author (this vol., p. 904), their products of reduction and subsequent oxidation were investigated. The former yields under these conditions thymoquinone, thus indicating a relative position of the groupings, thus :



The latter yields hydroxythymoquinone, showing that the groupings are in the relative position  $\text{Me} : \text{N}_2\text{Ph} : \text{OH} : \text{Pr} : \text{N}_2\text{Ph} = 1 : 2 : 3 : 4 : 5$ .  
V. H. V.

**Phenylazocarvacrol and Diphenylazocarvacrol.** By G. MAZZARA (*Gazzetta*, 15, 214—219).—On adding potassium nitrite to a dilute aqueous solution of aniline in hydrochloric acid, and pouring the product into a solution of carvacrol, there is gradually formed a yellowish precipitate, separable by treatment with potash solution into a soluble portion, *phenylazocarvacrol*  $\text{OH} \cdot \text{C}_6\text{H}_4\text{MePr} \cdot \text{N}_2\text{Ph}$ , and an insoluble portion, the corresponding *diphenyl* derivative,



The former separates from benzene in large yellowish-red crystals, melting at 80—85°, and yielding thymoquinone on reduction and subsequent oxidation, thus showing that the groupings

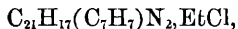


are in the positions 1 : 2 : 4 : 5. The latter forms silky brown needles, melting at 126°, and yielding diamidocarvacrol when reduced. Its constitution is probably expressed thus:  $\text{Me} : \text{OH} : \text{N}_2\text{Ph} : \text{Pr} : \text{N}_2\text{Ph} = 1 : 2 : 3 : 4 : 5$ .  
V. H. V.

**Amarine.** By A. CLAUS and H. KOHLSTOCK (*Ber.*, 18, 1849—1855).—*Diamarine silver nitrate*,  $(\text{C}_{21}\text{H}_{13}\text{N}_2)_2 \cdot \text{AgNO}_3 + \text{H}_2\text{O}$ , is obtained by the prolonged action of a solution of amarine in dilute alcohol on silver nitrate; it forms large brilliant prismatic crystals, which become opaque on keeping; it is insoluble in water and ether, but dissolves readily in alcohol and chloroform; it melts at 175° (uncorr.), and is decomposed by heating to a higher temperature, lophine and metallic silver being formed; acids convert it into the corresponding silver and amarine salts. The alcoholic solution of the compound is decomposed by potash, amarine, potassium nitrate, and the silver-derivative of amarine (*Abstr.*, 1883, 982) being formed; the latter may be more readily prepared by shaking an ammoniacal solution of silver oxide with a slight excess of an alcoholic solution of amarine—air and light being excluded. It forms a loose, white, crystalline powder, practically insoluble in all solvents with the exception of ammonia and chloroform, which dissolve small quantities. It melts at 218° (uncorr.), and is decomposed at a higher temperature. It is also decomposed by dilute acids; by prolonged heating with alcoholic potash, it is converted into amarine and silver oxide. Monobenzylamarine, obtained by the action of benzyl bromide on the silver compound (*loc. cit.*), may be prepared in the crystalline state by converting it into a salt and removing the tar, &c., with ether; the pure salt thus

obtained is treated with alkalis, and the base is obtained in tufts of needles insoluble in water but dissolving readily in ether, chloroform, &c.; it melts at 123—124° (uncorr.).

*Monobenzylamarine hydrochloride*,  $C_{21}H_{17}(C_7H_7)N_2.HCl$ , obtained by the action of hydrochloric acid on the base, forms a crystalline mass insoluble in ether, and only very slightly soluble in chloroform and water, but readily in alcohol; the platinochloride contains  $2\frac{1}{2}$  mols.  $H_2O$ . The *dichromate*,  $(C_{28}H_{24}N_2)_2.H_2Cr_2O_7$ , is obtained by the action of potassium dichromate on a dilute acetic acid solution of the base as a reddish-yellow, granular crystalline powder; it melts at 90°, and is readily soluble in alcohol, by which, however, it is partially decomposed. It is practically insoluble in water and ether. By boiling the salt with acetic acid it is decomposed, benzoic acid and amarine, with possibly a trace of lophine, being formed. *Benzylamarine oxalate*,  $(C_{28}H_{24}N_2)_2.H_2C_2O_4$ , is precipitated on adding an ethereal solution of oxalic acid to an ethereal solution of the base; it is readily soluble in alcohol, but insoluble in water and ether; it melts at 240° (uncorr.). *Benzylamarine benzylchloride* may be prepared by heating alcoholic solutions of benzylamarine and benzyl chloride in a reflux apparatus for 10—12 hours. *Benzylamarine ethiodide*,  $C_{21}H_{17}(C_7H_7)N_2.EtI$ , prepared by heating the alcoholic solutions of benzylamarine and ethyl iodide in molecular proportion, crystallises from alcohol in brilliant rhombic tablets which become yellow by the action of light and air; it is readily soluble in chloroform, but only slightly in water and ether; it melts at 182° (uncorr.). *Benzylamarine ethylchloride*,



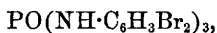
is obtained by the action of freshly precipitated silver chloride on the iodine compound; it crystallises from alcohol and chloroform in colourless plates, melts at 125° (uncorr.), and is insoluble in ether and water. The *platinochloride* of benzylamarine ethylchloride,



is thrown down from the alcoholic solution of the chloride on the addition of platinum chloride as a heavy bright-yellow precipitate; it is insoluble in water and alcohol, and melts at 152°; it is decomposed by heating above 200°. Benzylamarine ethiodide and chloride are not acted on by boiling ammonia solution, and are saponified by alcoholic potash. *Ethylbenzylamarine*,  $C_{21}H_{16}(C_7H_7)EtN_2$ , crystallises from alcohol in thin colourless plates; it is readily soluble in the usual solvents, with the exception of water; it melts at 135° (uncorr.); the *hydrochloride* is very similar to the isomeric benzylamarine ethylchloride, but is more readily soluble in alcohol, and melts at about 135° (uncorr.); its *platinochloride*,  $[C_{21}H_{16}(C_7H_7)EtN_2]_2.H_2PtCl_6$ , contains no water of crystallisation, and is of a darker colour. The corresponding methyl-derivatives of benzylamarine were also prepared. *Methylbenzylamarine* could not be obtained in the crystalline form. *Benzylamarine methiodide* crystallises in a felted mass of small needles; it melts at 130° (uncorr.); the corresponding chloride differs from the isomeric hydrochloride of methylbenzylamarine in being less readily soluble in chloroform.

A. P.

**Anilides of Orthophosphoric Acid.** By A. MICHAELIS and H. v. SODEN (*Annalen*, **229**, 334—340).—*Orthophosphoric anilide*,  $\text{PO}(\text{NHPh})_3$ , first prepared and described by Schiff (*Annalen*, **101**, 302), crystallises in six-sided rhombic plates. The crystals melt at  $208^\circ$ . The anilide dissolves in acetone, glacial acetic acid, and in hot alcohol, and is not decomposed by boiling hydrochloric acid, but it is easily attacked by oxidising agents. The *hexabromide*,



obtained by the action of bromine on the acetic acid solution, crystallises in silky needles melting at  $252^\circ$ . It is sparingly soluble in benzene, chloroform, carbon bisulphide, acetic acid, and strong sulphuric acid. It is practically insoluble in alcohol, ether, water, and light petroleum.

By the action of aniline (2 parts) on phosphorus oxychloride (1 part), the chloride  $\text{PO}(\text{NHPh})_2\text{Cl}$  is produced, together with aniline hydrochloride. If the crude product is poured into water and the residue treated with sodium hydroxide, sodium dianilido-phosphate will be formed. On the addition of hydrochloric acid to the solution, *dianilidorthophosphoric acid*,  $\text{PO}(\text{NHPh})_2\text{OH}$ , is precipitated as a white powder melting at  $196^\circ$ . It is soluble in alcohol and acetic acid, and is decomposed by boiling with water or with acids. The *silver salt* crystallises in needles soluble in water.

Monanilidophosphoric acid has not yet been prepared.

W. C. W.

**Triphenylphosphine and its Derivatives.** By A. MICHAELIS and H. v. SODEN (*Annalen*, **229**, 295—334).—The preparation of triphenylphosphine has been previously described by Michaelis (*Abstr.*, 1882, 1287). The pure compound forms colourless monoclinic prisms or plates freely soluble in ether, benzene, chloroform, and acetic acid. It melts at  $79^\circ$  and boils above  $360^\circ$ . Triphenylphosphine readily unites with 2 atoms of chlorine, bromine, or iodine, but it does not combine with carbon bisulphide. With hydriodic acid, it forms *triphenylphosphonium iodide*,  $\text{PPh}_3\text{I}$ . This compound crystallises in colourless prisms, soluble in alcohol, ether, and glacial acetic acid. It is decomposed by water. It melts at  $215^\circ$  with partial decomposition. The *platinochloride*,  $(\text{PPh}_3)_2\text{H}_2\text{PtCl}_6$ , is an amorphous compound insoluble in water and alcohol. It melts to a resinous mass when warmed.

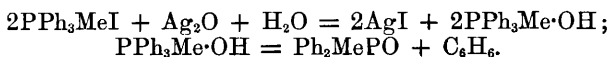
Triphenylphosphonium oxide, hydroxide, and sulphide and nitrotriphenylphosphonium oxide have been previously described (*Abstr.*, 1882, 1063, and 1884, 1180).

*Triphenylphosphine selenide*,  $\text{PPh}_3\text{Se}$ , formed by the direct union of triphenylphosphine with selenium, is deposited from alcohol in silky needles, melting at  $183^\circ$ . It dissolves freely in carbon bisulphide, benzene, chloroform, and hot acetic acid. The compounds of triphenylphosphine with methyl iodide, methylene iodide, and ethylene bromide have been previously described by the authors (*loc. cit.*).

*Triphenylethylphosphonium iodide*,  $\text{PPh}_3\text{EtI}$ , prepared by boiling triphenylphosphine with an excess of ethyl iodide, crystallises in colourless plates melting at  $165^\circ$ .

*Triphenylpropylphosphonium iodide*,  $\text{PPh}_3\text{PrI}$ , is deposited from a hot aqueous solution in needles, and from an alcoholic solution in thick plates belonging to the monoclinic system. The crystals are transparent, and possess considerable refractive power. They melt at  $201.5^\circ$ . The corresponding *isopropyl iodide* contains 2 mols.  $\text{H}_2\text{O}$ ,  $\text{PPh}_3(\text{CHMe}_2)\text{I} + 2\text{H}_2\text{O}$ . It crystallises in rhombic plates melting at  $191^\circ$ . *Triphenylisobutylphosphonium iodide*,  $\text{PPh}_3(\text{C}_4\text{H}_9)\text{I}$ , crystallises in needles or plates. It melts at  $176^\circ$ , and is freely soluble in alcohol. *Triphenylisoamylphosphonium iodide*,  $\text{PPh}_3(\text{C}_5\text{H}_{11})\text{I}$ , forms colourless prisms which melt at  $174^\circ$ .

The preceding compounds, on treatment with oxide of silver, yield a diphenylalkyl oxide and benzene:—

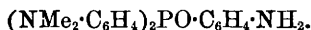


The oxides are inodorous. They dissolve freely in alcohol, chloroform, and benzene, and boil without decomposition at temperatures above  $360^\circ$ .

*Diphenylmethylphosphine oxide*,  $\text{Ph}_2\text{MePO}$ , crystallises in prisms melting at  $110^\circ$ . The *ethyl* compound,  $\text{Ph}_2\text{EtPO}$ , melts at  $121^\circ$ . Diphenylmethyl- and diphenylethyl-phosphines have been previously described (Abstr., 1882, 306). *Diphenylisoamylphosphine oxide*,  $\text{Ph}_2\text{C}_5\text{H}_{11}\text{PO}$ , melts at  $96^\circ$ .

Triphenylphosphine unites with benzyl chloride to form *triphenylbenzylphosphonium chloride*,  $\text{PPh}_3(\text{C}_7\text{H}_7)\text{Cl} + \text{H}_2\text{O}$ , a crystalline compound soluble in alcohol and water. It melts at  $287^\circ$ . The *bromide* is less soluble in water than the chloride. It melts at  $274^\circ$ . The *iodide* is sparingly soluble in water. It is deposited from alcohol in colourless prisms melting at  $253^\circ$ . The *nitrate*,  $\text{PPh}_3(\text{C}_7\text{H}_7)\cdot\text{NO}_3$ , is precipitated, when nitric acid is added to an aqueous solution of the chloride. It crystallises in needles or prisms which melt at  $203^\circ$  with decomposition. The nitrate requires 304.27 times its weight of water at  $15^\circ$  for complete solution. The *picrate*,  $\text{PPh}_3(\text{C}_7\text{H}_7)\cdot\text{OC}_6\text{H}_4(\text{NO}_2)_3$ , is very sparingly soluble in alcohol and in water. It is deposited from hot acetic acid solution in golden needles melting at  $148^\circ$ . The *dichromate* forms red needles insoluble in water and sparingly soluble in alcohol. The *thiocyanate* forms colourless prisms. It is soluble in alcohol and in hot water, and melts at  $189^\circ$ . Trinitro- and triamido-phenylphosphine oxide and their derivatives have been previously described (Abstr., 1884, 1180).

By the action of methyl iodide on the amide, a compound is obtained from which ammonia liberates the base



If a mixture of methyl alcohol and iodide is used, a hexamethylated base,  $(\text{NMe}_2\cdot\text{C}_6\text{H}_4)_3\text{PO}$ , is produced. It melts at  $150$ — $152^\circ$ .

On adding bromine-water to a solution of triamidotriphenylphosphine oxide in hydrochloric acid, *hexabromotriamidotriphenylphosphine oxide*,  $(\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Br}_2)_3\text{PO}$ , is thrown down as a brown precipitate. The compound is soluble in acids, but is reprecipitated on the addition

of water. It dissolves freely in acetone, and melts at about  $205^{\circ}$  with decomposition.  
W. C. W.

**Preparation of Metachlorobenzaldehyde.** (*Dingl. polyt. J.*, 257, 34.)—The following process has been patented by the *Farbwerke, vormals Meister, Lucius, and Brüning*:—50 parts of metanitrobenzaldehyde are reduced with 225 parts stannous chloride dissolved in 300 parts of hydrochloric acid. The mass is then diluted with water, cooled to  $0^{\circ}$ , and treated with 23 parts of sodium nitrite dissolved in 20 parts of water. The diazo-chloride contained in the solution is converted into metachlorobenzaldehyde by treatment with a hot solution of cuprous chloride in hydrochloric acid. On distilling the mixture with steam metachlorobenzaldehyde is liberated. D. B.

**Methyl Paraxylyl Ketone.** By A. CLAUS and R. WOLLNER (*Ber.*, 18, 1856—1861).—*Methyl paraxylyl ketone*,  $C_8H_8 \cdot COMe$ , is obtained by acting on paraxylene with acetic chloride in presence of aluminium chloride at the normal temperature. The reaction must be stopped before completion, as otherwise tarry and resinous compounds are formed. The ketone may be obtained pure by repeated fractioning, and forms a colourless mobile very refractive liquid, having a peculiar but not unpleasant aromatic odour. It boils at  $224-225^{\circ}$  (uncorr.). It is not solidified by cooling to  $14^{\circ}$ ; its sp. gr. = 0.9962 at  $19^{\circ}$ ; its vapour-density was found to be 4.93 (air = 1). It is practically insoluble in water, but dissolves readily in most other solvents; it also dissolves in concentrated acids, from which it is precipitated unaltered on the addition of water or alkalis. It may be distilled with steam. It does not form any compound with the acid sulphites of the alkalis. An attempt to obtain a hexamethyltriphenylbenzene by the condensation of the ketone by passing a stream of hydrogen chloride through the warm liquid did not prove successful, not a trace of any crystalline compound being formed even after the gas had been passed continually for two months.

The ketone may be readily oxidised by nitric acid (sp. gr. 1.12), two acids being formed; the first is Jacobsen's iso-xylic acid (*Abstr.*, 1882, 187); the second appears to be the  $\beta$ -xylic acid, obtained by the further oxidation of iso-xylic acid (*loc. cit.*) by potassium permanganate. The same oxidation products are obtained on treating methyl paraxylyl ketone with moderately concentrated chromic mixture, or with hot potassium permanganate solution. If, however, the ketone is acted on in the cold with dilute permanganate solution, *paraxylyl-glyoxylic acid*,  $C_6H_3Me_2 \cdot CO \cdot COOH$ , is obtained as a thick yellow oil, which after prolonged desiccation over sulphuric acid forms a crystalline mass; this melts between  $70^{\circ}$  and  $80^{\circ}$ , dissolves readily in the usual solvents with the exception of water, and is decomposed into carbonic anhydride and the aldehyde of iso-xylic acid by heating above  $200^{\circ}$ . With phenol and sulphuric acid, a cinnabar-red substance is produced; this yields a deep red solution with alkalis, from which it is again precipitated by acids. The acid is readily oxidised by nitric acid into xylic acid. The sodium and potassium salts of paraxylyl-glyoxylic acid are readily soluble in water and alcohol, but their



solutions are easily decomposed by heat or excess of alkali, benzaldehyde being formed. The *calcium* salt,  $(C_6H_5 \cdot CO \cdot COO)_2Ca + 3H_2O$ , and the *barium* salt,  $(C_6H_5 \cdot CO \cdot COO)_2Ba + 6H_2O$ , were also prepared; the *silver* salt,  $C_6H_5 \cdot CO \cdot COOAg$ , is obtained as a crystalline precipitate. Most of the heavy metals form insoluble salts with this acid. The *ethyl* salt,  $C_6H_5 \cdot CO \cdot COOEt$ , may be prepared by passing hydrogen chloride through an alcoholic solution of the acid. It is a light mobile very refractive liquid. By the action of sodium amalgam on a solution of the acid in dilute alcohol, a new acid is obtained, which is probably *parazylylhydroxyacetic acid*,



By heating 2 parts of xylylglyoxylic acid with 5 parts of acetic anhydride and 5 parts of sodium acetate for some time, another acid is obtained, which is manifestly dimethylcinnamic acid. It crystallises in needles, melts at  $132^\circ$  (uncorr.), and is readily soluble in hot water, ether, and petroleum. It sublimes above its melting point in short thin needles.

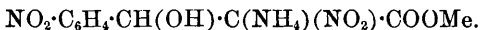
A. P.

**Phenylcinnamylacrylic Acid and Diphenyldiethylene.** By O. REBUFFAT (*Gazzetta*, **15**, 105—107).—Phenylcinnamylacrylic acid,  $CHPh : CH : CH : CPh \cdot COOH$ , prepared by heating cinnamaldehyde and sodium phenylacetate with acetic anhydride at  $170^\circ$ , crystallises in long glistening needles melting at  $187$ — $188^\circ$ . Its *silver* salt forms a white flocculent precipitate. On heating the acid at a temperature above its point of fusion, it is decomposed into carbonic anhydride and *diphenyldiethylene*,  $CHPh : CH : CH : CHPh$ , which is also obtained as a subsidiary product in the formation of the acid. This hydrocarbon crystallises in micaceous scales melting at  $147$ — $148^\circ$ , and boiling at  $320$ — $340^\circ$ .

V. H. V.

**Nitration of Cinnamic Acid Derivatives.** By P. FRIEDLÄNDER (*Annalen*, **229**, 203—210).—Theoretical.

**Nitration of Paranitrocinnamic Acid.** By P. FRIEDLÄNDER and J. MÄHLY (*Annalen*, **229**, 210—232).—*Ethyl paradinitrocinnamate*,  $NO_2 \cdot C_6H_4 \cdot CH : C(NO_2) \cdot COOEt$ , was obtained from the mononitro-derivative by the action of nitric and sulphuric acids; it melts at  $109$ — $110^\circ$ . The *methyl* salt melts at  $127^\circ$ . Both salts dissolve readily in benzene and chloroform, &c., sparingly in water and in light petroleum. They are converted by hydrochloric acid into paranitrobenzaldehyde and hydroxylamine; water also decomposes them. When treated with hydrobromic acid, they form additive compounds. Dilute soda acts on the alkyl salt with formation of a compound,  $C_{14}H_{10}N_2O_8$  or  $C_{14}H_{11}N_2O_8$ , melting at  $188^\circ$ . When treated with ammonia, a product is obtained which yields very unstable salts; this compound is probably a salt of *methyl paranitrophenyl- $\alpha$ -nitro- $\beta$ -lactate*,



When methyl dinitrocinnamate is crystallised from methyl alcohol, an additive compound, *methyl paranitrophenyl- $\beta$ -methoxynitropro-*

propionate,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CH}(\text{NO}_2)\cdot\text{COOMe}$ , is formed; it melts  $9-10^\circ$  lower than the original compound. The alcohol so taken up cannot be separated without entire decomposition of the substance. Analogous compounds were prepared. *Methyl paranitrophenyl- $\beta$ -ethoxynitropropionate* melts at  $110^\circ$ ; it crystallises in monoclinic prisms,  $a : b : c = 0.8489 : 1 : 0.5170$ .  $\beta = 87^\circ 25'$ . *Ethyl paranitrophenyl-methoxynitropropionate* melts at  $77^\circ$ . *Ethyl paranitrophenylethoxynitropropionate* forms monoclinic prisms,  $a : b : c = 2.7475 : 1 : ?$ ; it melts at  $52^\circ$ . These compounds are much more stable than the corresponding salts of dinitrocinnamic acid; they do not unite with hydrobromic acid. An ammonium salt was made, from which several metallic salts, all very unstable, were prepared.

*Dinitrocinnamic acid,*

$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH} : \text{C}(\text{NO}_2)\cdot\text{COOH}$  [ $\text{NO}_2 : \text{CH} : \text{C}(\text{NO}_2)\cdot\text{COOH} = 1 : 4$ ],

was obtained by the nitration of mononitrocinnamic acid at a temperature between  $-20^\circ$  and  $-10^\circ$ ; it dissolves readily in the usual solvents. The aqueous solution at  $0^\circ$  evolves carbonic anhydride, and yields *dinitrostyrolene*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH} : \text{CH}\cdot\text{NO}_2$ . The latter compound is sparingly soluble in the usual solvents; it crystallises from glacial acetic acid in yellow plates melting at  $199^\circ$ . Alcoholic potash dissolves it with formation of a compound,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OEt})\cdot\text{CH}_2\cdot\text{NO}_2$ . When heated with sulphuric acid at  $100^\circ$ , it decomposes into carbonic oxide, hydroxylamine, and paranitrobenzaldehyde.

When ethyl dinitrocinnamate is reduced, paramidophenylalanine and paramidophenyl cyanide are formed (comp. Abstr., 1883, 918; 1884, 757). N. H. M.

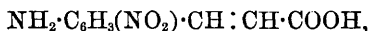
**Nitration of Meta- and Ortho-nitrocinnamic Acids, Orthamidocinnamic Acid, Carbostyryl, and Paramidocinnamic Acid.** By P. FRIEDLÄNDER and M. LAZARUS (*Annalen*, 229, 233—247).—*Dinitrostyrolene*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH} : \text{CH}\cdot\text{NO}_2$ , is formed by the action of nitric and sulphuric acids on metanitrocinnamic acid at a temperature below  $0^\circ$ ; carbonic anhydride is evolved during the reaction. It forms yellow plates sparingly soluble in hot water and in alcohol, but dissolves more readily in benzene, ether, and chloroform, and melts at  $122^\circ$ . It closely resembles the dinitrostyrolene obtained from paranitrocinnamic acid (see preceding Abstract) in its behaviour.

When ethyl metanitrocinnamate is treated with the nitrating mixture at a temperature below  $20^\circ$ , it is converted into *ethyl dinitrocinnamate*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH} : \text{C}(\text{NO}_2)\cdot\text{COOEt}$ . The latter compound is readily soluble in the usual solvents, insoluble in water and in light petroleum. From its ethereal solution, it separates in thick lustrous plates. It resembles the paradinitro-compound closely (see preceding Abstract). When a solution of *ethyl dinitrethyllactate* (obtained by warming ethyl dinitrocinnamate with ethyl alcohol) in dilute soda is treated with bromine-water, a compound, *metanitrophenylethoxydibromonitroethane*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OEt})\cdot\text{CBr}_2\cdot\text{NO}_2$ , melting at  $98-99^\circ$ , is formed. An analogous compound melting at  $145-146^\circ$  was obtained from the methoxylated ethyl salt. The same compounds were obtained

by dissolving nitrostyrolene in ethyl and methyl alcohol respectively, adding dilute soda, and precipitating with bromine-water.

When ethyl metadinitrocinnamate is reduced, a very unstable amido-acid is formed, together with a small quantity of a base, probably *metamidobenzyl cyanide*.

By the nitration of orthamidocinnamic acid, two isomerides were obtained; the chief product,  $\alpha$ -nitro-orthamidocinnamic acid,



forms brownish-red needles melting at  $240^\circ$ , insoluble in benzene, light petroleum, and ether, readily soluble in alcohol and acetone, and sparingly soluble in water. When heated with hydrochloric acid at  $150^\circ$ , it is converted into  $\alpha$ -nitrocarbostyryl, which crystallises from alcohol in almost white needles and does not melt at  $320^\circ$ . The second compound obtained from orthamidocinnamic acid, namely,  $\beta$ -nitro-orthamidocinnamic acid,  $\text{C}_9\text{H}_8\text{N}_2\text{O}_4$ , forms brownish-yellow crystals which melt at  $254^\circ$ . It is almost insoluble in dilute mineral acids, whilst the  $\alpha$ -compound dissolves readily in them. Hydrochloric acid at  $150^\circ$  acts on it with formation of  $\beta$ -nitrocarbostyryl melting at  $260^\circ$ .

When ethyl nitroorthamidocinnamate is nitrated, it yields  $\beta$ -nitrocarbostyryl and ethyl  $\alpha$ -nitroorthamidocinnamate melting at  $158$ — $160^\circ$ .

Carbostyryl when nitrated yields  $\gamma$ -nitrocarbostyryl. The latter compound melts at  $280^\circ$ , is sparingly soluble in alcohol, more readily in glacial acetic acid. When reduced,  $\gamma$ -amidocarbostyryl, a sparingly soluble yellow substance which does not melt at  $320^\circ$ , is formed.

Paramidocinnamic acid when nitrated yields *nitroparamido- $\omega$ -nitrostyrolene*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CH} : \text{CH} \cdot \text{NO}_2$ . This substance crystallises from alcohol in fine reddish-brown needles. An acetyl derivative melting at  $250$ — $252^\circ$  was prepared.

N. H. M.

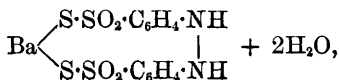
**Salts of Salicylic Acid.** By H. MILONE (*Gazzetta*, **15**, 219—228).

—The *barium* salt,  $(\text{C}_7\text{H}_5\text{O}_2)_2\text{Ba} + \text{H}_2\text{O}$ , crystallises in concentrically grouped silky needles, sparingly soluble in cold, more soluble in hot water. The *calcium* and *strontium* salts crystallise with  $2\text{H}_2\text{O}$ ; the *magnesium* salt crystallises with  $4\text{H}_2\text{O}$  in silky needles, the *zinc* salt with  $2\text{H}_2\text{O}$ , the *cadmium* salt with one  $\text{H}_2\text{O}$ . The *manganese* salt forms pink crystals containing  $2\text{H}_2\text{O}$ , which rapidly turn brown with separation of manganese peroxide.

V. H. V.

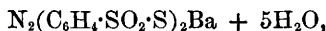
**Azobenzenethiosulphonic and Azobenzenesulphinic Acids.**

By R. BAUER (*Annalen*, **229**, 353—371).—When metazobenzene-disulphonic chloride is slowly added to a well-cooled concentrated solution of barium sulphhydrate, *barium hydrazobenzenedithiodisulphonate* is deposited as a white powder, and *barium azobenzenedithiodisulphonate* remains in solution. The former salt,



is soluble in hot water, but the solution oxidises on exposure to the air. The addition of hydrochloric acid precipitates the free acid from the solution. The acid is sparingly soluble in water and insoluble in alcohol. Potassium permanganate oxidises the solution of the barium salt, potassium azobenzenedisulphonate being formed. This salt crystallises with 2 mols.  $\text{H}_2\text{O}$  in reddish-yellow needles, and with 4 mols.  $\text{H}_2\text{O}$  in plates. The barium salt is also decomposed by mercuric oxide, yielding mercuric sulphide and azobenzenemonothiodisulphonate.

*Metazobenzenedithiodisulphonic acid*,  $\text{HS}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{SH}$ , is deposited from its salts on the addition of glacial acetic acid; mineral acids cannot be used for this purpose. The acid melts at  $91^\circ$ , and is insoluble in alcohol and water. The *barium salt*,



dissolves in hot water, but is partially decomposed by recrystallisation, with formation of azobenzenemonothiodisulphonate and separation of sulphur. The *sodium* and *ammonium* salts dissolve freely in water and alcohol. The ammonium salt is deliquescent. Aqueous solutions of these salts give amorphous precipitates with copper, lead, silver, and ferric salts. On oxidation with potassium permanganate, potassium sulphate and azobenzenedisulphonate are formed.

*Metazobenzenemonothiodisulphonic acid*,  $\text{HS}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{H}$ , is obtained as an amorphous precipitate, insoluble in alcohol and sparingly soluble in water, when a mineral acid is added to a solution of any of the salts of this acid. The acid melts below  $100^\circ$ . The *barium* salt is formed when a solution of barium hydrazobenzenedithiodisulphonate or azobenzenedithiodisulphonate is evaporated. It is sparingly soluble in water. The *potassium* salt dissolves freely in water and in alcohol of 95 per cent. The *sodium* salt is freely soluble in water, but less soluble in alcohol. It crystallises in needles. The lead, copper, silver, and ferric salts can be obtained in the form of amorphous precipitates.

The mono- and di-thiosulphonic acids yield resinous products when boiled with acids, but they are converted into sulphinic acids by the action of sodium amalgam.

*Metazobenzenedisulphinic acid*,  $\text{HSO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{H}$ , is soluble in alcohol and in hot water. The *sodium* and *lead* salts crystallise in needles which dissolve freely in water. The *barium* salt,  $\text{N}_2(\text{C}_6\text{H}_4\cdot\text{SO}_2)_2\text{Ba}$ , is sparingly soluble in water, and insoluble in alcohol. The lead, copper, and silver salts are insoluble in water. Potassium permanganate converts the azobenzenedisulphinates into azobenzenedisulphonates, and concentrated ammonium sulphide converts them into azobenzenedithiodisulphonates. When the acid is treated with concentrated hydrochloric acid at  $100^\circ$ , about 2 per cent. of it is converted into a base, probably  $\text{HSO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{H}$ . This base is soluble in hot alcohol. The *hydrochloride* dissolves freely in alcohol and water. The *hydrobromide* crystallises in prisms soluble in alcohol and in water. Azobenzenedisulphinic acid on reduction with stannous chloride also yields a base which appears to have the same composition as hydrazobenzenedisulphinic acid.

The following compounds were obtained from parazobenzene-disulphonic chloride (m. p. 222°).

*Parazobenzenedithiodisulphonic acid*  $\text{HS}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{SH}$ , melts below 100°. It is sparingly soluble in water and alcohol. The *barium* salt,  $\text{N}_2(\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{S})_2\text{Ba}$ , is soluble in hot water, and is decomposed by recrystallisation. It is not acted on by ammonium sulphide. The *sodium* salt forms efflorescent crystals, which dissolve freely in alcohol and in water. The lead, copper, ferric, and mercuric salts are insoluble in water.

*Parazobenzenedisulphinic acid*,  $\text{HSO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{H}$ , is sparingly soluble in water and alcohol. It forms a *barium* salt, which is almost insoluble in cold water. The *sodium* salt crystallises with 4 mols.  $\text{H}_2\text{O}$  in yellow scales. It dissolves readily in water, and the solution gives amorphous precipitates with solutions of lead, silver, copper, mercuric and ferric salts. W. C. W.

**Diamidomethoxytriphenylmethane.** By G. MAZZARA and G. POSSETTO (*Guzzetta*, 15, 57—59).—By heating anisaldehyde with aniline in presence of hydrochloric acid, *diamidomethoxytriphenylmethane*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ , is formed. It separates from its solution in toluene in the form of a pink crystalline crust, melting at 65°, and containing 1 mol. of toluene. Its platinumchloride is a yellow amorphous substance, soluble in alcohol. V. H. V.

**Essence of Lemon.** By G. BOUCHARDAT and J. LAFONT (*Compt. rend.*, 101, 383—385).—The authors have carefully fractionated essence of lemon and examined the products obtained by the action of dry hydrogen chloride on the different fractions. In most cases distillation was conducted under reduced pressure. The results lead to the conclusion that essence of lemon is a highly complex substance consisting mainly of hydrocarbons of the composition  $\text{C}_{20}\text{H}_{16}$ , and a little cymene. The most abundant of the  $\text{C}_{20}\text{H}_{16}$  hydrocarbons is a citrene, which boils at about 178°, has a rotatory power higher than + 105°, and yields directly a solid inactive dihydrochloride. The essence also contains small quantities of several terebenthenes, which begin to boil below 162°, and yield monohydrochlorides differing from one another in their rotatory powers. C. H. B.

**Crystallographic Properties of Camphor-derivatives.** By P. CAZENEUVE and J. MOREL (*Compt. rend.*, 101, 438—440).—Camphor crystallises in hexagonal prisms terminated by hexagonal pyramids, but the monohaloid derivatives crystallise in the monoclinic system and are isomorphous one with another. It follows that hydrogen is not crystallogenically equivalent to the halogens by which it is displaced, but the latter may be regarded as equivalent to one another, although the equivalence is not absolute.

The bi-substitution-derivatives of camphor crystallise in the rhombic system, and are all isomorphous. The crystallogenic equivalence between chlorine and bromine seems to persist in this series, although the differences become more marked, but the introduction of the  $\text{NO}_2$ -group produces still more marked divergencies.

Zinc nitro-camphor,  $(C_{10}H_{14}O \cdot NO_2)_2Zn$ , appears to crystallise in rhombic prisms quite distinct from those of the ordinary bi-derivatives.

In the original paper, measurements of the different angles and faces are given.  
C. H. B.

**Barosma Crenata.** By P. SPICA (*Gazzetta*, **15**, 195—202).—The therapeutic value of extract of leaves of the *Barosma crenata* or buchu in chronic diseases of the genito-urinary organs and in catarrh seems to depend on the presence of an ethereal oil and an exceedingly bitter resin. Flückiger (*Pharm. J. Trans.*, 1880, 219), in an investigation of the allied species, *Barosma betulina*, obtained a crystalline substance and an oil. On extracting the leaves with ether and subsequent distillation, an oil is obtained, separable by potash into a soluble and an insoluble portion (eleoptene). Hydrochloric acid precipitates from the former a crystalline substance, best separated by solution in ether.

The *eleoptene* is a colourless oil boiling at 204—206°, resembling peppermint in odour; the results of analyses seemed to indicate that this compound is an isomeride of borneol,  $C_{10}H_{18}O$ ; on distillation with sodium, it is converted into a phenolic substance,  $C_8H_{12}O$ ; this is a slightly yellowish oil, sparingly soluble in water, and resembling thymol in taste and odour.

The crystalline substance (*stearoptene*) mentioned above, forms long colourless monoclinic needles, partially subliming at 82° and boiling at 220° with decomposition. Analyses pointed to a formula,  $C_5H_8O$ , probably  $C_{10}H_{16}O_2$ , or an oxycamphor ( $C_{14}H_{22}O_3$ , Flückiger). It appears probable that this substance is a phenylic ether containing a phenolic hydroxyl grouping.  
V. H. V.

**So-called Isophloridzin.** By H. SCHIFF (*Annalen*, **229**, 371—376).—Rochleder (*Zeit. f. Chem.*, 1868, 711) obtained a glucoside from the leaves of the apple tree, which he considered to be distinct from phloridzin. The author points out that this so-called isophloridzin does not differ in any of its characteristic properties from ordinary phloridzin. The chief point of difference consists in the greater solubility of isophloretin in ether, but the author has shown that the solubility of phloretin in ether is increased by the presence of small quantities of alcohol or water in the solvent.

W. C. W.

**Identity of Regianin and Juglone.** By T. L. PHIPSON (*Chem. News*, **52**, 39).—The author points out the identity of Mylius's juglone with regianin extracted from fresh green walnut husks by himself in 1868. He suggests that the latter name should be retained, modified if necessary.  
D. A. L.

**The Red Colouring Matters of Wine and Vegetables.** By TERREIL (*Bull. Soc. Chim.*, **44**, 2—6).—The red colouring matter of wine and of the skin of black grapes, plums, gooseberries, raspberries, mulberries, elderberries, also of the flowers of the corn poppy, mallows, and roses, are precipitated from their solutions by an excess

of hydrochloric acid, slowly at the ordinary temperature, but rapidly on boiling. The precipitate always contains an ulmic substance, from which the colouring principle may be dissolved out by alcohol; thus obtained, it forms brittle varnish-like scales, insoluble in water and ether, but readily soluble in alcohol, forming a brownish-red solution with a slightly yellowish tinge; acids change this colour to an intense red, whilst alkalis give a green coloration changing rapidly to a brownish-yellow on exposure to the air.

The red colouring matters of the beetroot and the fruit of the *Phytolacca decandra* are not precipitated by hydrochloric acid, but on boiling with it, first become more brilliant, then change to a violet, and finally turn a brownish-yellow.

The red colouring matters of logwood and other dyewoods and of orcein are precipitated by hydrochloric acid, but the precipitate is soluble in boiling water and dissolves in dilute alkalis with a violet coloration, which becomes brown on exposure to the air.

The colouring principle of the cochineal is also precipitated by hydrochloric acid; the precipitate is soluble in dilute alkalis, forming a violet solution of a more brilliant colour than that furnished by the dyewoods, and it turns brown more slowly on exposure to the air.

Litmus yields a precipitate with hydrochloric acid, which is soluble in alcohol with a red colour, and in dilute alkalis with a permanent blue colour.

A. P.

#### Action of Heat on Acetopyrroline and Carbonylpyrroline.

By G. CIAMICIAN and P. MAGNAGHI (*Ber.*, **18**, 1828—1832).—Acetopyrroline is converted into pyrrol methyl ketone by heating at 250—280° in a sealed tube, and the formation of dipseudacetopyrroline by heating pseudacetopyrroline with acetic anhydride (this vol., p. 378) may be explained by the previous formation in this manner of pyrrol methyl ketone, which is then converted into dipseudacetopyrroline by the acetic anhydride.

When acetopyrroline is heated with benzoic anhydride no benzoyl compound is obtained, as had been expected, but a small quantity of benzamide is formed. The melting point of pure benzamide was found to be 130°, and not 128° as previously stated (*Ber.*, **10**, 1785); it forms a white crystalline precipitate with silver nitrate and ammonia.

By heating carbonylpyrroline in a sealed tube for some hours at 250° it is converted into dipyrrol ketone (this vol., p. 809), which crystallises in the trimetric system:  $a : b : c = 2.53109 : 1 : 2.90144$ , the chief forms occurring being (110) (101) and (102).

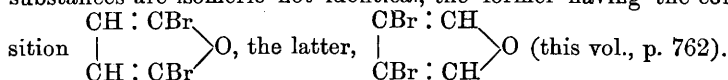
A second compound, *pyrrolyl-pyrroline*,  $C_4H_4N \cdot CO \cdot C_4H_4N$ , also isomeric with carbonylpyrroline, is formed at the same time; it is obtained in white flakes having a silky lustre, it has the same melting point as carbonylpyrroline (62—63°), but differs from it in its appearance and crystalline form and cannot be distilled with steam; it also forms a yellow crystalline precipitate with silver nitrate and ammonia, which probably has the composition  $C_4H_4N \cdot CO \cdot C_4H_3NAg$ , whilst carbonylpyrroline reduces ammoniacal silver nitrate solution. The three isomeric compounds (carbonylpyrroline, pyrrolylpyrroline, and

dipyrrolyl ketone) may be further distinguished from one another by the action of potash: dipyrrolyl ketone is not acted on, carbonyl pyrroline is decomposed into carbonic anhydride and pyrroline, whilst pyrrolyl-pyrroline is resolved into pyrroline and  $\alpha$ -carbopyrrolic acid. The authors point out that pyrroline-derivatives containing acid radicles in the imidogen-group are converted into more stable ketonic compounds by the action of heat, in which these radicles are united directly with the carbon.

A. P.

**Reciprocal Transformation of the Pyrroline, Furfuryl, and Thiophene Groupings.** By F. CANZONERI and V. OLIVER (*Gazzetta*, **15**, 113—117).—After allusion to the analogy in constitution between pyrroline, thiophen, and furfuran, a description is given of attempted experiments made with a view of transforming a member of one group into that of another. On distilling ammonium monobromopyromucate,  $C_4H_2Br\text{-CONH}_2$ , is produced, crystallising in glistening needles, melting at  $146^\circ$ , sparingly soluble in cold, more soluble in hot water, alcohol, ether, and benzene.

If dibromopyromucic acid (1 part) is distilled with calcium hydroxide (2 parts) at  $200^\circ$ , dibromofurfuran,  $C_4H_2Br_2O_2$ , is produced, a yellowish liquid of ethereal odour, boiling at  $165\text{--}167^\circ$ . Although the boiling point of this compound is nearly coincident with that of the dibromofurfuran described by Hill and Hartshorn, yet the two substances are isomeric not identical, the former having the composition



V. H. V.

**Pyridinetricarboxylic Acid.** By C. BÖTTINGER (*Annalen*, **229**, 248).—A controversial note.

**$\alpha$ -Metadiquinolines.** By W. V. MILLER and F. KINKELIN (*Ber.*, **18**, 1900—1915).—When 50 grams of metanitrocinnamaldehyde (this vol., p. 791), 30 grams of aniline, and 100 grams of concentrated hydrochloric acid are heated together for about three hours until the temperature of the mixture reaches  $140^\circ$ , the bright yellow needles of the hydrochloride of the anilide first formed are converted into a dark-brown melt. From this *metanitrophenylquinoline*,  $C_{15}H_{10}N_2O_2$ , was isolated. It crystallises in colourless needles which melt at  $124^\circ$ , and are sparingly soluble in cold ether or alcohol, easily in boiling alcohol and benzene. It is a feeble base yielding, with strong acids, salts which are decomposed by water. The *hydrochloride* forms unstable crystals, the *platinochloride*,  $(C_{15}H_{10}N_2O_2)_2 \cdot H_2PtCl_6$ , sparingly soluble plates, and the *picrate* small unstable plates. When treated in alcoholic solution with tin and hydrochloric acid it yields *metamidophenylquinoline*. This crystallises in long glistening needles which melt at  $120^\circ$ . It is sparingly soluble in light petroleum and in cold water, easily in boiling water and in ether, benzene, and methyl alcohol. It forms two series of salts, the neutral being colourless, the basic of an intense yellow. The *platinochloride*, when prepared from a hot hydrochloric solution of the base, forms a dark yellow crystalline powder of the

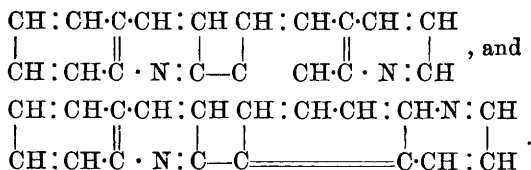


formula  $C_{15}H_{12}N_2 \cdot H_2PtCl_6$ . From a cold solution, platinum chloride precipitates long, thin needles, which approximate in composition to the formula  $(C_{15}H_{12}N_2)_2 \cdot H_2PtCl_6$ . A solution of the latter salt, when boiled, gives a crystalline precipitate of the former salt.

*Metanitrophenylhydroquinoline*,  $C_{15}H_{14}N_2O_2$ , was obtained in small quantities as a bye-product in the preparation of metanitrophenylquinoline. It crystallises in colourless needles melting at  $71^\circ$ , and gives Liebermann's nitroso-reaction. When treated with tin and hydrochloric acid, it yields *metamidophenylhydroquinoline*. This substance was more easily obtained by boiling metamidophenylquinoline with tin and hydrochloric acid for 2 to 3 hours. Its *hydrochloride*,  $C_{15}H_{16}N_2 \cdot 2HCl$ , forms slightly reddish, monoclinic plates; its *platinochloride* a red amorphous precipitate. The free base is a thick syrup, which at  $100^\circ$  becomes liquid and gives off an unpleasant odour, but cannot be distilled. It reduces silver salts. Its hydrochloride, when treated with sodium nitrite, yields an amorphous, orange nitroso-compound.

*Metahydroxyphenylquinoline*,  $C_{15}NH_{10} \cdot OH$ , was obtained from the amido-quinoline by means of the diazo-reaction. It crystallises in long needles which melt at  $156^\circ$ , and are easily soluble in alcohol and ether. It is soluble in acids and alkalis with yellow coloration. The *sulphate* and *hydrochloride* form unstable, yellow needles, the *platinochloride* plates, and the *sodium-derivative* glittering yellow scales. When distilled with zinc-dust it yields  $\alpha$ -phenylquinoline (Abstr., 1883, 1148 and 1149). The nitrophenyl-group in the original substance is therefore in the  $\alpha$  (or 2) position in the pyridine-ring. The author points out the similarity of constitution and dissimilarity in reactions between metamidophenylquinoline and flavaniline. O. Fischer and Rudolph explain the non-reducibility of flavaniline as due to the amido-phenyl-group occupying the  $\alpha$ -position in the pyridine nucleus, but as metamidophenylquinoline with a similar constitution is very easily reducible, this explanation cannot be correct.

When metamidophenylquinoline (20 grams) is heated with glycerol (70 grams), concentrated sulphuric acid (60 grams), and orthonitrophenol (15 grams), two isomeric  $\alpha$ -meta-diquinolines,  $C_{18}N_2H_{12}$ , are obtained. The one melting at  $159^\circ$  crystallises from alcohol in small rectangular plates belonging to the monoclinic system. It is sparingly soluble in ether, alcohol, and benzene, and cannot be distilled. Its *hydrochloride*,  $C_{18}H_{12}N_2 \cdot 2HCl + 2H_2O$ , forms scales, the *sulphate* concentrically grouped needles, the *platinochloride* a heavy, crystalline powder, the *picrate* a crystalline powder melting at  $240^\circ$ , and the *methiodide* a yellow crystalline powder. No dimethiodide could be obtained. The other isomeride melts at  $115^\circ$ , and forms pale yellow, triclinic prismatic crystals. It is easily soluble in alcohol, benzene, and ether, sparingly so in light petroleum. The *hydrochloride*,  $C_{18}H_{12}N_2 \cdot 2HCl + 3H_2O$ , forms easily soluble plates, the *platinochloride* a crystalline powder, the *picrate* a gelatinous precipitate, and the *chromate* concentrically grouped prisms. These two compounds must have the constitutions represented by the formulæ—



but which formula belongs to each must be decided by further investigation.

The authors point out that in the syntheses hitherto performed by Skraup's reaction, only one of the two possible isomerides has been obtained.

L. T. T.

**Relation of Brucine to Strychnine.** By A. HANSEN (*Ber.*, 18, 1917—1918).—By the oxidation of a solution of strychnine in dilute sulphuric acid with chromic mixture, the author has obtained the same compound,  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_4$ , which he obtained by a similar oxidation of brucine (this vol., p. 819). It is thus clear that brucine and strychnine must both contain the nucleus  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2$ , and that their difference must be due to the groups  $\text{C}_7\text{H}_8\text{O}_2$  and  $\text{C}_5\text{H}_4$ , which are respectively removed by oxidation. The author considers that the group  $\text{C}_5\text{H}_4$  lost by strychnine must be part of a phenyl-group attached to the  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2$  group by one carbon. This view is strengthened by the fact that strychnine forms a nitro-derivative, whilst the oxidation compound,  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_4$ , does not. The group  $\text{C}_7\text{H}_8\text{O}_2$ , lost by brucine, is probably part of a dimethoxyphenyl-group; and brucine is thus probably a dimethoxystrychnine.

L. T. T.

**Putrefaction Bases (Ptomaines) from Fish.** By O. BOCKLISCH (*Ber.*, 18, 1922—1927).—It has been found (this vol., p. 566) that the putrefaction alkaloids obtained from cod are different from those obtained from perch. The author has now investigated the putrefaction bases obtained from the herring. Ordinary herring pickle was found to contain choline, trimethylamine, dimethylamine, and methylamine. 30 lbs. of fresh herrings were allowed to putrefy for twelve days. The alkaline putrefying magma was then acidified with hydrochloric acid, diluted with about three times its volume of water, boiled (to coagulate albumin), and filtered. The filtrate was evaporated, the syrupy residue dissolved in alcohol, and alcoholic mercuric chloride added. The precipitate formed was found to contain cadaverine and putrescine (both of which have already been described by Brieger in his pamphlet on ptomaines), and traces of trimethylamine and methylamine. The filtrate from the mercuric precipitate contained trimethylamine, methylamine, and a small quantity of a base which is probably Brieger's gadinine. The author calls attention to the large quantity of trimethylamine and methylamine obtained, the latter substance not having hitherto been detected amongst the putrefaction bases from fish.

L. T. T.

**Albuminoids and the Coagulation of Colloids.** By E. GRIMAUX (*Bull. Soc. Chim.*, 44, 21—25).—This is a reply to some criticisms made by Gautier (this vol., p. 1082) on the author's views.

**Ferric Peptonate.** By M. ROBIN (*Compt. rend.*, **101**, 321—322).—

A solution of peptone is mixed with a certain quantity of officinal ferric chloride, glycerol added, and then excess of ammonia. A precipitate of ferric hydroxide is at first formed, but this redissolves in a slight excess of ammonia, yielding a clear transparent liquid, which is neutral to litmus-paper, and gives no reaction with potassium ferrocyanide or ferricyanide. If, however, the liquid is acidified with hydrochloric acid the Prussian blue reaction is readily obtained, and the reaction is also given by a mixture of ferric chloride with peptone to which no glycerol has been added. If either the peptone or the glycerol is omitted, a clear solution cannot be obtained on adding ammonia; moreover, the glycerol must be added before the ammonia.

The solution of ferric peptonate is perfectly dialysable, and the product can be mixed with blood or any alkaline substance without any decomposition taking place. 7 grams of the peptonate were administered to a dog through the rectum, potassium ferricyanide being administered through the stomach at the same time. The coagulated blood of the animal showed no blue coloration, but the colour was easily obtained on adding a few drops of hydrochloric acid to the urine.

C. H. B.

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## Physiological Chemistry.

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**Quantitative Relationship of Pepsin to Peptones.** By E. SCHÜTZ (*Zeit. physiol. Chem.*, 9, 577).—In his experimental investigation of this question, the author employs a pepsin solution prepared from the stomach of the pig, which is caused to act, under carefully regulated conditions, on a 1 per cent. solution of egg albumin, previously freed from globulin by treatment with hydrochloric acid. By the addition of a small quantity of thymol, 0.2 gram previously dissolved in 1 c.c. alcohol, to 1000 c.c. of the albumin solution, it is kept from decomposition, and serves for a long series of determinations. Experiments proved that the thymol was without influence on the digestion, so long as the quantity added was less than 0.01 per cent. The determinations of the resulting peptone were made by the optical method, the solution being previously freed from other albuminoids by precipitation with ferric chloride in presence of sodium acetate. Three series of determinations, yielding concordant numbers, established a simple numerical relationship between the quantities of peptone and pepsin, the peptone being formed in the ratio of the square root of the quantity of pepsin taken. Taking as an arbitrary pepsin unit, viz., the quantity necessary to produce 1 gram peptone under the conditions postulated by the author, the number of these units in 1 c.c. of the pepsin solution investigated, is deduced by means of the equation—

$$P = \frac{1}{p} \left( 4 \times \frac{m}{39^{\circ} 18'} \right)^2,$$

$p$  being the number of cubic centimetres of pepsin solution employed in the experiment,  $m$  the actual rotation in minutes, and  $39^{\circ} 18'$  being the rotation corresponding to 1 gram peptone, as determined by the author's experiments.

The error due to the presence of sugar in the albumin, that is, in the peptone solution, is determined by optical examination of the solution after precipitating the peptones by means of phosphomolybdic acid.

C. F. C.

**Assimilation of Fats.** By I. MUNCK (*Zeit. physiol. Chem.*, **9**, 568).—This is a critical discussion of the recent paper of Landwehr's (*ibid.*, p. 361), in which, having described a peculiar animal gum contained in and easily isolated from the pancreas, and also formed by the action of bile upon mucin, he assigns to it, on account of its remarkable power of emulsifying fats, an important part in promoting their absorption in the intestines. This the author shows, on the evidence, to be over estimated. In the first case, the emulsifying power of the gastric juice has been overlooked. The presence of fat acids in the intestines, and their disappearance during the passage to the anus, which he maintains in opposition to Landwehr, he regards as normal to the digestive process. Landwehr's observations on his own incapacity for absorbing fat acids by intestinal digestion, not having been conducted quantitatively, cannot be regarded as disproving the results of the author's repeated experiments on the dog: further, they introduce the uncertain factor of individual idiosyncrasy. Moreover, the supply of fat acids in the mass, to the intestines, introduces a condition altogether abnormal. Landwehr's hypothesis of the liberation of fat acids, as a result of the putrefactive resolution of the intestines, has little weight against the positive evidence afforded by the researches of Grützner (*Arch. Ges. Physiol.*, **12**, 285) and Cash (*Arch. Physiol.*, 1880, 32) on the saponification of the fats in gastric and pancreatic digestion. In regard to the reactions of the intestines and their contents, the author cites evidence showing that the acid reaction obtains during a much greater length than is allowed by Landwehr, and therefore the emulsifying power of the animal gum is thus far inoperative; moreover, the absorption of non-emulsified fat is an established property of the lymph cells of the adenoid tissue of the intestine, and it is generally accepted that emulsification is not an essential preliminary to the absorption.

However sound, therefore, Landwehr's observations on the animal gum may be in themselves, they cannot be taken as materially affecting the position of fat absorption.

C. F. C.

**Further Researches on the Digestion of the Horse.** By ELLENBERGER and HOFMEISTER (*Bied. Centr.*, 1885, 366—368).—The rapidity with which the albuminoids are dissolved is dependent on the amount of ferment present; the action is assisted by alkalis but diminished by acids. Alkaline salts, especially sodium carbonate, aid the fermentation; trypsin works best at  $35$ — $50^{\circ}$ , and its action is not destroyed by cold or dehydration, but is by heat. This ferment is not present in the glands as such, but as lymphogen, and it converts

albuminoids first into hemialbuminose, then into peptone. The neutral fats are capable of being decomposed by the fat ferment, and the lactic ferment is found only in traces in the pancreas. All the ferments of the gastric glands can be separated by alcohol from an extract of those glands, and bear drying without change, neither is the moderate addition of phenol or salicylic acid detrimental to their action. This extract dissolves oats, flesh, and cheese, but not cartilage, sinew, horns, and bones; raw flesh is more readily dissolved than boiled. Tyrosine and leucine are formed during pancreatic digestion. It appears that the pancreatic juice combines in its solvent action that of all the other digestive fluids.

E. W. P.

**Feeding with Dry and Steeped Indian Corn.** By MÜLLER (*Bied. Centr.*, 1885, 379—380).—Dry corn is better as a food for sheep than if steeped; the reason is probably that soaked corn calls for a smaller formation of the digestive fluids than the untreated grain, consequently it remains in the paunch for a shorter time.

E. W. P.

**Ensilage Maize for Cows.** By ROSE (*Bied. Centr.*, 1885, 374—375).—The green maize was mixed with one-twelfth of chopped straw and then siloed; of this mixture each cow received 30 kilos., together with oil-cake and wheat chaff. The yield of milk was thereby raised; the butter was of a yellow colour and of good taste. Müller considers that this ensilage should be allowed to cool in the silo before use. Klein has found in maize ensilage as much as 2 per cent. of acetic and lactic acids.

E. W. P.

**Value of Sugar as Food for Stock.** By M. MÄRCKER (*Bied. Centr.*, 1885, 375—379).—Sugar is of no value as a fattening food for sheep; on the other hand it may be given to pigs with great advantage.

E. W. P.

**The Albuminoids of Milk.** By A. DOGIEL (*Zeit. physiol. Chem.*, 9, 591).—1. *Peptones*.—As a result of his investigation of cow's milk, Schmidt-Mülheim states that it contains peptones, the proportion varying from 0.08 to 0.19 per cent. of the milk (*Pflüger's Archiv*, 28, 287). Hofmeister, on the other hand, denies that they are present, and in human milk likewise (*Zeits. physiol. Chem.*, 2, 288). In further investigating this question, the author sought first to ascertain the probable error inherent in the method of isolating the peptones. For this purpose known quantities of peptones were added, and the milk was then treated with ferric chloride solution in the usual way for the separation of other proteids; the peptones were estimated in the filtrate by means of a comparative colorimetric determination based on the biuret reaction. In 19 experiments in which 40 c.c. of milk were taken for each, the quantities of peptones added varied from 0.004 to 0.020 gram, and the solutions finally obtained, after precipitation and washing, amounted to 190—250 c.c. The ultimate result was to show that the quantity of peptone retained by the precipitate was independent of the amount added, the quantity lost being approximately 0.005 in each experiment, that is, 0.0023 for every

100 c.c. solution ultimately obtained. That the peptone is retained by the precipitate is proved, according to the author, by the diminished loss which is noted when the iron oxide precipitate is boiled with water, and this aqueous extract added to the solution. By varying the quantity of milk, it was found that the loss of peptone remained equally uninfluenced.

On the basis of the experience of these blank experiments, the author proceeded to the examination of normal specimens of cow's and woman's milk, adopting special precautions in the isolation by precipitation of the peptones presumed to be present. In all cases, however, negative results were obtained. Having further repeated Schmidt-Mülheim's experiments (*loc. cit.*), and found that the substance supposed by him to be a peptone is a residue merely of one of the normal proteids of milk, the author finally concludes that these milks do not contain peptones.

2. *Caseïns*.—The author has isolated, with special precautions, the caseïns from woman's and from cow's milk for the purpose of instituting a comparison of their properties. Having found that their reactions were substantially identical, he examined the products of their artificial (peptic) digestion, which proved to be identical also, and there can be no doubt therefore that they are, chemically, very closely related.

3. *Other Proteïds*.—In a comparative examination of the products of peptic digestion of the two milks, by the optical method, the author found the rotation to be 50 per cent. greater in the case of the products from woman's milk, whence he concludes that in regard to the proteïds, not peptones, the two milks are differently composed. He suggests that the difference may be chiefly in respect of the lactoalbuminoid recently described by Sebelien (*ibid.*, 9, 403).

C. F. C.

**Chemical Changes in the Eggs of Bombyx Mori during Development.** By A. TICHOMIROFF (*Zeit. physiol. Chem.*, 9, 566).—In his recent communication on this subject (*ibid.*, 518) the author has overlooked a paper by Verson (*Bolletino Mens. di Bachicoltura*, 1884, 9), containing an analysis of the chorion of these eggs, upon the results of which it was stated to consist of keratin. The author points out that the method of isolation and purification adopted by Verson is not calculated to give a homogeneous product, and he sees no occasion therefore to modify the view which he has expressed.

C. F. C.

**Relation between Atomic Weight and Physiological Function.** By F. SESINI (*Gazzetta*, 15, 107—109).—It is here remarked that none of the elements of atomic weight greater than 56 are indispensable or even useful for vegetable economy. This appears to be a more or less proximate consequence of the smaller condensation of matter within the elementary atoms, which are thus endowed with the necessary mobility for their assimilation and transformation within the organism. Of the elements of higher atomic weight some, such as bromine and iodine, appear in marine plants, and have no well-defined physiological function, whilst the remainder, especially arsenic, zinc, and lead, are distinctly poisonous.

V. H. V.

**Poisoning by Hydrogen Sulphide.** By P. BROUARDEL and P. LOYE (*Compt. rend.*, **101**, 401—404).—Dogs were allowed to breathe mixtures of air and hydrogen sulphide containing 2 per cent. and 0·5 per cent. of the latter gas. In the first case, death occurred in two or three minutes; in the second case in from 17 to 50 minutes. A detailed account of the symptoms in both cases is given in the paper. There appear to be two kinds of poisoning by hydrogen sulphide, one in which death is sudden, and is due to action on the nervous centres; the other in which death takes place more slowly, and is due to a combination of asphyxia and action on the nervous centres. The poisonous action is due rather to the tension of the hydrogen sulphide in the atmosphere than to the quantity actually inhaled.

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C. H. B.



## Chemistry of Vegetable Physiology and Agriculture.

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**Oxidation and Reduction under the Influence of Microscopic Organisms in the Soil.** By A. MÜNTZ (*Compt. rend.*, 101, 248—250).—The author has already shown (this vol., p. 870) that in presence of air and the nitric ferment in soils, iodides are converted into iodates. He now finds that alkaline bromides are converted into bromates under the same conditions, but similar experiments with chlorides gave no definite results.

In presence of the nitric ferment, but out of contact with air, alkaline iodates, bromates, and chlorates are completely and somewhat rapidly reduced to iodides, bromides, and chlorides respectively.

C. H. B.

**Glycogen in Beer Yeast.** By L. ERRERA (*Compt. rend.*, 101, 253—255).—The cells of *Saccharomyces cerevisiæ* in active growth contain glycogen in considerable proportion. Sometimes the entire cell-contents consist of this substance, which doubtless plays the same part as starch in the higher plants. The presence of glycogen explains many earlier observations respecting yeast, for instance, that it yields sugar when boiled with dilute acids.

C. H. B.

**Self-fermentation of Yeast.** By V. LEHMANN (*Zeit. physiol. Chem.*, 9, 563).—The author has investigated the changes in the composition of the yeast substance, in regard to the resolution of nucleïn into its basic constituents, hypoxanthine, xanthine, and guanine, which accompany the process of self-fermentation. The quantities of these bases were determined as products of resolution by boiling the yeast with dilute sulphuric acid (I) in the original yeast (300 grams); (II) after standing diffused in water (100 c.c.) for 24 hours at the ordinary temperature; (III) after digestion under the same conditions as in (II), but at the temperature of 38—40°.

The results of two series of experiments are contained in the following table, in which the quantities of guanine and xanthine are given jointly:—

	I.	II.	III.
Hypoxanthine .....	0·2101	0·2188	0·0212
Guanine and xanthine.....	0·0902	0·0871	0·1324

	I.	II.	III.
Hypoxanthine .....	0·1606	0·1736	0·0239
Guanine and xanthine.....	0·0383	0·0509	0·1337

At the ordinary temperature, therefore, traces only of these bases are liberated; at the higher temperature (III), on the other hand, the quantity of hypoxanthine suffers diminution, that of guanine and xanthine being increased.

C. F. C.

**Selective Fermentation of Invert Sugar.** By H. LEPLAY (*Compt. rend.*, 101, 479—482).—A criticism of Bourquelot and Maumené's recent papers on selective fermentation (this vol., p. 1003, and 1085). The author maintains the accuracy of Dubrunfaut's observations.

C. H. B.

**The Succinic Acid Ferment and its Action on Cane-sugar.** By J. F. TEIXEIRA (*Bied. Centr.*, 1885, 493—494).—By this ferment is understood the microbe which develops in dilute solutions of ammonium tartrate and nutritive salts, converting them into the ammonium salts of carbonic, acetic, formic, and especially succinic acids. The author has succeeded in cultivating pure growths. Under the microscope the bacteria appear from 0·6—0·001 mm. diameter, and from 2·5 to 0·004 mm. long. They are mobile and are furnished with processes, at the ends of which accumulations of plasma are visible; pure mineral solutions are not favourable to development; cabbage soup with 3 per cent. of glycerol is the best culture fluid. In different media, the bacterium appears to assume different forms; in sour milk, beer wort, and urine with 10 per cent. sugar, it takes a cylindrical form; in old beef extract, weak Liebig extract, in cabbage soup, with or without glycerol, and in asparagine solutions it is longer, and resembles a bacillus. The ferment assumes very peculiar but irregular shapes on the surface of 3 per cent. cane-sugar solutions to which a little flesh-broth has been added. Strong acids prevent its development, and air is very injurious, long keeping is also unfavourable; a temperature of 41·5° is advantageous, but if it reaches 60° development is arrested. The action of the bacterium on cane-sugar is slow, but its products are the same as in the decomposition of tartaric acid, with the addition of alcohol. Sugar manufacturers need not dread the ferment, their operations requiring a temperature of 60°, which kills it.

J. F.

**Electrical Researches.** By HOLDEFLEISS (*Bied. Centr.*, 1885, 392—393).—The object of the researches was to determine what influence, if any, was exerted on a crop of roots and potatoes by a weak galvanic current passing through the soil. In the field, copper plates, 50 by 80 cm. square, were sunk vertically, so that one plate covered two drills; the plates were 56 m. distant, and were connected with 14 Meidinger elements. A further experiment consisted of a combination of zinc and copper plates without a battery, placed at

a distance of 33 m. apart; lastly, a third experiment was made with another arrangement of pairs of plates, whereby a stronger current was produced. Results: a constant current was observed; no influence seems to have been exerted on the growth of the crop as regards quality or quantity, when under the influence of the first arrangement; under the second set of conditions, the crop at first was forwarded, but not later on; an increase in yield amounting to 15—24 per cent. was remarked in the latter case.

E. W. P.

**Deviation of Roots from the Normal Varieties of Growth (Aërotropism).** By H. MOLISCH (*Bied. Centr.*, 1885, 402—403).—Roots partly in water experience an irregular mutation; after slight immersion they grow more or less horizontally, and even turn to the surface of the water; this is probably due to the different amounts of oxygen present in the various layers. Experiments were made with maize and peas, and it was so arranged that they should receive different quantities of oxygen on opposite sides; the roots either bent away from the richer atmosphere, or during the first two hours they bent towards it, and then away from it. This action is explained by the “retarding influence exerted by oxygen on the linear growth of the concave side.” According as gases cause a bending towards or from them, we have positive and negative aërotropism. The action is more marked when carbonic anhydride, chlorine, &c., is used instead of oxygen.

E. W. P.

**Gas contained in Floating and Submerged Leaves.** By N. GRÉHANT and J. PEYROU (*Compt. rend.*, 101, 485—486).—The authors have extracted, in a vacuum at 50° and 100° respectively, the gases contained in the floating and submerged leaves of various aquatic plants under different conditions of light, and have analysed the gases. The results show that the elements constituting the parenchyma of floating and submerged leaves live in an interior medium somewhat poor in oxygen. There is always a great difference, so far as regards the proportion of oxygen, between the gases extracted from the leaves, the surrounding atmosphere, and the gases extracted from the water. In bright sunshine, however, the proportion of oxygen in the leaves is considerably increased.

C. H. B.

**Formation of Sulphates in Germination.** By E. SCHULZE (*Zeit. physiol. Chem.*, 9, 616).—The author points out, in regard to a recent paper by Tammann on this subject (*ibid.*, 9, 416), that Kellner, whose statements on the question of the increase of sulphuric acid during the germination of peas are therein disproved, had himself already corrected what his later investigations (*Phytoch. Unters.*, 1, 58) had shown to be erroneous.

C. F. C.

**So-called Sour Rot of Grapes.** By K. PORTELE (*Bied. Centr.*, 1885, 403—404).—The caterpillar of the *Tortix uvana* does much damage to grapes; if it attacks the hard berry, the berry becomes acid and harder; if, however, sugar has formed in the berry, then many ferments are introduced into the mash, and the wine is deteriorated. If the worm attacks ripe berries, then *Pencillium glaucum* and *Asper-*

*gillus glaucus* form in the wound; the growth of this mildew may close up the entrance, when the whole contents of the berry rot, and quantities of bacteria are produced, which destroy the mycelium. If the opening remains open, the contents also decompose, *Saccharomyces ellips.* and *Saccharomyces aspiculatus* are produced, then alcohol is formed, which is again changed into carbonic anhydride and water, but more frequently into acetic acid. Should heavy rain fall, then these affected grapes will do no harm to the must, as they will be washed clean, and only the husks remain.

E. W. P.

**Influence of Calcium Sulphide on Barley.** By J. FITTBOGEN and others (*Bied. Centr.*, 1885, 385—392).—The material employed to ascertain the effect of calcium sulphide on the growth of barley was the ash of two sorts of brown coal, containing 3.85 and 2.74 per cent. respectively of the compound. A known quantity of artificially prepared sulphide was also used, mixed with the usual mixture of plant food, together with sand. In the earliest stages of growth, the harmful action was perceptible, and as growth proceeded the poisonous action showed itself by producing white and brown markings on the leaves, which markings gradually spread over the whole leaf. These spots, when microscopically examined, were found to indicate the cells which were empty and destitute of chlorophyll; moreover, the presence of calcium sulphide seemed to retard growth. This action seems to be due to the formation of sulphuretted hydrogen, produced by the medium of water, the oxygen of the soil also being removed from the service of the plants. It was thought probable that the calcium hydroxide formed by the decomposition of the sulphide might also prove detrimental; yet no harm seemed to arise from this compound when added within certain limits, consequently as the hydroxide formed by double decomposition lies within these limits, it is concluded that it exercises no influence.

E. W. P.

**Effect of Rain on the Quality of Hay.** By W. EUGLING (*Bied. Centr.*, 1885, 421).—Rain removes protein and amido-compounds, but increases the fibre, but this action only occurs when the hay has been first thoroughly wetted.

E. W. P.

**Valuation of Hay.** By F. SCHINDLER (*Bied. Centr.*, 1885, 459—463).—The ordinary method of judging the quality of hay is by its appearance and smell, no scientific mode of examination being known. The author proposes sorting the sample botanically into four qualities and weighing them, thus forming an approximately scientific standard. His classification is Graminaceæ, acid grasses, Leguminosæ, and refuse or weeds, the nutritive value standing in direct proportion to the quantity of Leguminosæ, and inversely to the acid grasses.

The system requires a good knowledge of the various kinds of grass.

J. F.

**Protection of Potatoes against Disease.** By J. L. JENSEN (*Bied. Centr.*, 1885 473—476).—The author defends his system of protecting potatoes against disease by earthing up the stalks; the

depth of earth must be at least 26 to 30 cm., so that when the tubers form they are covered with at least 10 to 12 cm. of soil, the drills not being nearer together than 80 cm., and the operation should be carried out some ten days before the flowering of the plants, or as soon as the stalks are strong enough to bear the additional weight of earth; as much as indicated should be put on, but not enough to bend the stalks.

From 105 experiments in Denmark, Norway, and Sweden the author concludes that when properly carried out, the health of the crop is greatly improved, and the yield not diminished. J. F.

**Desiccation of Seed Potatoes.** By ANDRAE (*Bied. Centr.*, 1885, 472—473).—Experiments on the loss of weight by four kinds of potatoes exposed on hurdles in a closed but ventilated chamber; the loss, naturally, was proportional to the increase of temperature, and the cut samples lost more than the whole tubers. J. F.

**Shaded and Unshaded Sugar-beets.** By B. LACH (*Bied. Centr.*, 1885, 394—396).—Sugar-beet grown under the shade of trees is neither so heavy in the crop nor so rich in sugar as beet grown in the open; but the shaded beet continues to produce sugar for a longer period than the other, because, being shaded, there is more moisture, the absence of which retards the further growth of the beet in the open. E. W. P.

**Cultivation and Composition of Sorghum.** By TROSCHKE (*Bied. Centr.*, 1885, 396—398).—Sorghum should be sown in May (Pomerania) in 18-inch drills, and thinned in July; blossoming commences on 1st September, and finishes on the 12th. The composition at the time of (1) thinning, (2) of blossoming, (3) of end of blossom, (4) of ripening of stem, is as follows:—

	(1.)	(2.)	(3.)	(4.)
Water .....	86.0	82.0	75.0	67.0
Ash .....	1.6	1.3	1.6	1.6
Albumin .....	3.4	2.6	2.8	2.7
Fibre .....	3.2	5.4	8.7	11.4
Cellulose, &c. ....	5.1	7.9	11.3	16.6
Fat .....	0.7	0.8	0.6	0.7
Nitrogen as albumin in the dry matter .....	17.9	12.4	7.8	6.5

The author recommends its use as green fodder.

E. W. P.

**Starch Refuse as Fodder.** By O. SAARE (*Bied. Centr.*, 1885, 465—467).—A great proportion of the nutritive matter in starch-waste is generally lost when ordinary means are employed for its utilisation. The author describes a process devised by Kette, a large

farmer, which he considers a great improvement. It is an arrangement by which the pulp is received from the machines and allowed to filter in heavy sacks suitably arranged, after which pressure is applied by means of wooden wedges; half the water is thus expressed. The substance is next mixed with the water from which the starch has been precipitated, and boiled for fodder. The result appears to be satisfactory. J. F.

**Influence of different Systems of applying Manures.** By C. v. TAUTPHÖUS and E. WOLLNY (*Bied. Centr.*, 1885, 447—459).—Experiments were made by the authors and others on the influence of various methods of applying manures, namely, saturating the soil with solutions of nutritive salts, manuring in drills, placing manure in the holes where plants are to be afterwards put, and transplanting roots into a mass of soil mixed with moist manures.

As far as can be learned from laboratory experiments, the authors favour the sowing of the manures in drills or spreading it broadcast, the other methods showing no advantages; the last-named, planting in a mass of moist earth and manure, was decidedly hurtful to the plants experimented on. J. F.

**Various Manure Materials.** By P. WAGNER and others (*Bied. Centr.*, 442—444).—Wool-dust is produced in large quantities; the spinning mills of Belgium alone offer annually 20,000,000 kilos., but the variations in its value are very considerable; in 29 samples examined by Wagner, the nitrogen ranged from 1.51 per cent. to 10.40 per cent., and he advises that the material should be purchased on the basis of its nitrogen contents, and great precautions taken in drawing the sample; he values the nitrogen in wool-dust at little more than half that of Chili saltpetre.

Tanners' offal consists in great measure of mineral matter, and its organic matter gives up its nitrogen with great difficulty. The ash contains traces of calcium sulphide which is injurious to the vegetation, but not to the extent generally suspected. The author considers this a good manure for meadows if spread in autumn, after having been treated with freshly-burnt lime and left covered up with earth for about two months.

Ground oil-cake refuse was found to contain nitrogen, 4.22; phosphoric acid, 1.8; potash, 0.8 per cent. The use of this manure is recommended for potatoes with the addition of superphosphate, and with sulphate of potash and magnesia for tobacco. Concentrated osmose-water has hitherto been considered injurious when applied to sugar-beets. A. Wagner, however, has obtained good results from its use. Six portions of land were sown, one treated heavily with stable manure, the other five with various proportions of concentrated osmose-water. The yield of these latter was larger, both in gross weight of root and net sugar, so that with proper precautions this material may be successfully employed as manure. J. F.

**Chili Saltpetre or Ammonium Sulphate.** By M. MÄRCKER (*Bied. Centr.*, 1885, 439—442).—The author regrets the large sums of

money sent out of Germany for the purchase of Chili saltpetre, and urges the use of ammonium sulphate of home manufacture as a substitute. He examines the relative values of the two substances as fertilisers, and refers to the experiments of Lawes and Gilbert, which show a slight inferiority in the results obtained by the use of the ammonium salt. He thinks that it can only successfully compete with sodium nitrate when it is so much lower in price that larger quantities can be used, and he looks forward to a time in the near future when the ammonia from coke-ovens and similar sources may be utilised cheaply, and so bring about such a condition of things. J. F.

**Sugar-beet and Phosphates.** By A. LADUREAU (*Bied. Centr.*, 1885, 361).—Roots grown on land containing 0.640 per 1000 (0.125 soluble in acetic acid) of phosphoric acid, were equally affected by the application of soluble or precipitated phosphates. E. W. P.

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## Analytical Chemistry.

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**Laboratory Apparatus for the Production of Uniform Temperatures.** (*Dingl. polyt. J.*, 256, 452—456.)

**Silver Iodide as a Blowpipe Reagent.** By P. CASAMAJOR (*Chem. News*, 52, 1—2).—The author proceeds as follows to obtain the iodide reaction with various metals before the blowpipe (compare Wheeler and Ludeking, this vol., p. 596). The substance is mixed into a paste with silver iodide and powdered charcoal, and the mixture is placed at one end of an open glass tube. On heating the mixture before the blowpipe, the deposition of iodide soon occurs. Characteristic deposits are formed with mercury, bismuth, iron, thallium, and molybdenum; lead and tin both give bright-yellow deposits. D. A. L.

**Lakmoïd and other Indicators.** By R. T. THOMSON (*Chem. News*, 52, 18—20, 29—32).—The author has made numerous experiments with lakmoïd, and compares it with the other indicators he has already investigated (compare Abstr., 1884, 691, 869, &c.). Blue and red lakmoïd-paper may be prepared in a manner similar to litmus-papers; the colour is fast, and does not wash out with water; the red is somewhat purple in tone, and is apt to deceive those accustomed to litmus-red. Lakmoïd may be used either in solution or as paper, but it is preferable in the latter form, especially with cold liquids. With regard to its delicacy, in the absence of interfering agents, lakmoïd ranks with rosolic acid, phenacetolin, and phenolphthaleïn, being somewhat superior to litmus and methyl-orange. Either in solution or as paper, it gives very delicate end reactions in the titration of alkali in pure hydroxides of Na, K,  $\text{NH}_4$ , Ca, and Ba, and in arsenites and silicates of Na and K, and in the estimation of free  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , or  $\text{HNO}_3$ .



with soda. In the estimation of alkali in carbonates and hydrogen carbonates of K, Na, and  $\text{NH}_4$ , very accurate results are obtained with lakmoïd-paper in the cold; red paper indicates the smallest trace of alkali, whereas the blue under such conditions is slightly affected by carbonic anhydride, but a few seconds' exposure to the air is sufficient to dispel the faint redness. Lakmoïd is applied to the estimation of the base in the carbonates of Ba, Ca, Mg, in the same fashion as the other indicators, that is, by adding excess of acid and titrating back with soda. The author supports Draper's statement (this vol., p. 931) as to the sensitiveness of lakmoïd towards calcium and magnesium carbonates, and recommends it for use in Hehner's method for determining hardness of waters as described (Abstr., 1884, 692). With sulphides, the liberated hydrogen sulphide bleaches lakmoïd; the blue colour is reproduced on adding excess of soda, but only to be bleached again when hydrogen sulphide is liberated. Lakmoïd-paper may, however, be used, and gives trustworthy results, the whole of the base in K, Na, and  $\text{NH}_4$  sulphides being estimated. With sulphites, the hydrogen sulphites, and with phosphates and arsenates the dihydrogen salts are neutral to lakmoïd; hence when this indicator is employed 50 per cent. of the base is determined in Na, K,  $\text{NH}_4$ , Ca, and Mg sulphites, and in Na, K,  $\text{NH}_4$ , and Ca hydrogen phosphates, or in Na, K, and  $\text{NH}_4$  hydrogen arsenates; litmus only indicates about 17 per cent. of soda in sodium sulphite, and about 13 per cent. in sodium phosphate. Lakmoïd is sensitive to the alkalinity of borates of K, Na,  $\text{NH}_4$ , Ca, Ba, and Mg, and hence resembles methyl-orange in this as well as in its action with phosphates, and in fact lakmoïd-paper may be used in preference to methyl-orange for the estimation of phosphoric acid, and for borates, when insoluble matter is present. Again, like methyl-orange, and unlike litmus, lakmoïd shows an alkaline reaction with alumina. Dichromates are neutral to lakmoïd, whilst chromates are alkaline; hence with this indicator we are able to determine the quantity of chromate or of free chromic acid in a sample of dichromate; the fastness of the colour is here turned to account, for the highly coloured chromate can be washed off the paper without affecting the lakmoïd colour. Sodium thiosulphate, ferrous, copper, and zinc sulphates, and ferrous and cupric chlorides, are all neutral to lakmoïd, whereas most of them are more or less alkaline or acid to litmus. Lakmoïd can therefore be used for determining free acid in commercial ammonium sulphate. Lakmoïd cannot be used for the estimation of oxalic, acetic, tartaric, or citric acids; litmus-paper is good for oxalic and tartaric acid, whilst phenolphthaleïn is the only good indicator for acetic and citric acids. With lactic acid, litmus gives accurate results, rosolic acid is satisfactory, but phenolphthaleïn is the most delicate; whilst phenacetolin, methyl-orange, and lakmoïd are useless. Fresh milk is alkaline to lakmoïd-paper, neutral to litmus, and acid to phenolphthaleïn. The alkalinity to lakmoïd and the acidity to phenolphthaleïn are each equal in extent to the alkalinity of the milk ash. Sour milk, even after three weeks, is still alkaline to lakmoïd, and it is only slightly acid to this indicator when thoroughly decomposed. With sour milk, litmus registers the acquired acidity; phenolphthaleïn indicates in addition the excess due to its sensitiveness

for fresh milk. Litmus must be used when neutralising milk before the extraction of the fat. Litmus is the best indicator for estimating the acidity of urine. Urine is alkaline to lakmoïd, and in fact this alkalinity is greater than its acidity for litmus. Strong alcohol does not interfere with the accuracy of phenolphthaleïn, phenacetolin, rosolic acid, or red lakmoïd-paper, but it impairs the delicacy of blue litmus-paper, of blue lakmoïd-paper, and of methyl-orange. Dilute alcohol does not affect these indicators. If, however, blue lakmoïd-paper is well immersed in alcohol, then withdrawn, and the alcohol evaporated from the paper by gently heating, any acid reaction will soon appear. With lakmoïd, phenol is neutral, and saliva is strongly alkaline. There is evidently a great difference between lakmoïd and litmus.

D. A. L.

#### **Dimethylamidoazobenzene as an Indicator in Alkalimetry.**

By B. FISCHER and O. PHILIPP (*Arch. Pharm.* [3], **22**, 434—438).—Methyl-orange is frequently employed as an indicator, but the variable composition of the commercial article has perhaps hindered its general application; moreover, the change in colour from orange to carnation-red is not very striking. These difficulties disappear when dimethylamidoazobenzene is used. This compound is easily prepared in the pure state; and the end reaction is indicated by a sharp change from lemon-yellow to carnation-red. To prepare the reagent, 9.3 grams (1 mol.) of aniline are dissolved in 30 grams (2 mols.) hydrochloric acid (25 per cent.), and the diluted and well-cooled liquid is treated with a solution of 7 grams (1 mol.) sodium nitrite in water, stirring well. In a short time, the liquid is poured into a solution of 12 grams (1 mol.) dimethylaniline in 15 grams hydrochloric acid, and after remaining a while sufficient sodium acetate (about 30 grams) is added to produce a distinct odour of acetic acid. The crystals which separate are recrystallised from alcohol; their melting point lies about 115°. For use, an alcoholic solution (1 : 200) is made up, and about five drops are added to each 100 c.c. of liquid to be titrated. Experiments detailed show the delicacy of the indicator. Carbonic acid does not affect the colour. The various acids give reds of different tints. Test-papers did not give good results, probably owing to the reagent being too strongly fixed by the fibre; but gypsum plates moistened with the alcoholic solution answered well.

J. T.

#### **Volumetric Estimation of Sulphur.**

By N. v. KLOBUKOW (*Ber.*, **18**, 1861—1869).—It is well known that nascent hydrogen reduces sulphurous anhydride to hydrogen sulphide, but its action on free sulphur has been but little investigated. The author finds that under suitable conditions finely-divided sulphur is completely converted into hydrogen sulphide by the action of nascent hydrogen, and proposes the following method (based on these reactions) for the estimation of the total sulphur in any substance decomposable by hydrochloric acid, in place of the troublesome method of oxidation at present employed.

A weighed quantity of the substance to be analysed is introduced into a decomposing flask with excess of granulated zinc (free from sulphur and arsenic) and a suitable quantity of water. The flask is

closed, and a stream of hydrogen passed through to displace all the air. Hydrochloric acid is then added slowly by means of a thistle funnel, and the evolved sulphuretted hydrogen passed into a known quantity of standard iodine solution. If free sulphur is liberated during the reaction, the flask should be cooled and the evolution of hydrogen moderated (as free sulphur is more easily acted on at a low temperature), but if only sulphurous acid is formed no cooling is necessary. Towards the end of the reaction the flask should be gradually heated to 70—80°. A slow current of hydrogen should be passed during the reaction, and a more rapid one when the whole of the zinc has been dissolved, so as to sweep out the last traces of hydrogen sulphide. The hydrogen sulphide is then estimated by titration. The sulphur liberated as sulphuric acid is of course not acted on by nascent hydrogen, and remains in the decomposing flask; it is estimated as barium sulphate in the usual way. The sum of the sulphur obtained as sulphate and as hydrogen sulphide gives the total sulphur present. The author has obtained very good results by this method, and considers it much quicker and more simple than the oxidation methods.

L. T. T.

**Examination of Iron and Steel.** (*Dingl. polyt. J.*, 256, 546—549.)—For the estimation of phosphorus in iron and steel, the molybdate method is preferred, as the magnesia method is deficient in accuracy for the determination of small quantities of phosphorus. The phosphorus present in the metal is weighed as ammonium phospho-molybdate, using the precautions recommended by Finkener (*Abstr.*, 1879, 275). On evaporating the nitric acid solution and gently igniting the residue as described by Finkener, a higher percentage of phosphorus (as much as 30 per cent. more) is obtained than when the residue is not heated above 100°, a circumstance which, although not yet explained, should not be disregarded.

In order to estimate titanium in iron and its ores, Ledebur (*Chem. Zeit.*, 1885, 483) employs the following method:—2 to 5 grams of ore are treated with concentrated hydrochloric acid and evaporated to dryness on the water-bath. The residue is heated with a small amount of hydrochloric acid, diluted with water, filtered, and washed with cold water. The residue on the filter is dried, fused with sodium and potassium carbonates, the mass dissolved in water, treated with an excess of hydrochloric acid, and evaporated on the water-bath. To the residue, concentrated hydrochloric acid is added, the mixture is heated gently for a time, then diluted with cold water, filtered, and washed with cold water. The two filtrates are mixed together, and generally contain all the titanous acid, so that the silica on the filter dissolves completely when boiled with sodium carbonate. The titanous acid solution is treated with sufficient sulphuric acid to convert all chlorides present into sulphates, and is evaporated to expel all the hydrochloric acid. After cooling, the solution is diluted with water, treated with sulphurous acid or hydrogen sodium sulphite, and heated gently to reduce the iron present. The solution is then neutralised with sodium carbonate, so that no permanent precipitate forms, and is heated to boiling for two hours. The evaporated water is replaced from time to time, and small quantities of hydrogen sodium sulphite are added

to prevent oxidation. The total titanous acid is thus precipitated, also the phosphoric acid and some iron. The solution is filtered, and the precipitate washed with water. It is then dried, fused with sodium and potassium carbonates, and treated with water, whereby the phosphoric acid is dissolved; the residue, containing sodium titanate and ferric oxide, is treated with sulphuric acid, boiled, diluted with water, reduced with hydrogen sodium sulphite, neutralised with sodium carbonate, and the titanous acid precipitated by boiling for two hours as before. The precipitate, which should be quite colourless, is filtered, washed, ignited, and weighed. To determine titanium in pig iron, 15 grams are dissolved in nitric acid, evaporated, and heated to eliminate carbon compounds and expel nitric acid. The residue is dissolved in concentrated hydrochloric acid, diluted with water, and filtered. The residue on the filter, after washing and drying, is fused with sodium carbonate and potassium nitrate, the silica separated by evaporation with hydrochloric acid, and the process continued as above described.

D. B.

**Estimation of Carbon in Iron and Steel.** By T. TURNER (*Chem. News*, 52, 15—17).—In the process recommended, iron is dissolved in cupric chloride, steel in hydrochloric acid; the solution is filtered through a tube-filter, constructed in the manner described below, and the residue burnt in the same tube in a current of air. The filter is made from a piece of combustion-tube drawn out at one end; the total length of the piece of tube is 11 inches, the wide part being 8 inches long. The constricted aperture is closed by a small baked clay pea. Upon this about half an inch of pure sand is placed, then follows a small plug of asbestos, and about a quarter of an inch of sand. The other simple but necessary arrangements and apparatus are fully described in the paper. Good results have been obtained.

D. A. L.

**Estimation of Sulphur in Steel and Iron.** By J. PÉTER (*Bull. Soc. Chim.*, 44, 16—17).—10 grams of the sample are dissolved in hydrochloric acid, at first in the cold and finally at 100°, the gases disengaged being passed through a depth of about 10 centimetres of a solution of potassium permanganate (50 to 60 grams per litre) contained in an ordinary test-glass. After all evolution of gas has ceased, 20 c.c. of pure hydrochloric acid are added to the permanganate solution, and the whole boiled until the potassium permanganate is reduced. The sulphuric acid in the almost colourless solution is then estimated in the usual way by means of barium chloride. Should the sample of iron contain a very high percentage of sulphur, it is advisable to take only 5 or even 2 grams, and to add a small quantity of pure soda to the permanganate solution. The results given by this method are very satisfactory, agreeing completely with those obtained by oxidation with potassium chlorate and hydrochloric acid. Silica is never found in the precipitate, even when operating with a ferrosilicon containing 12 per cent. of silicon. Absorption-tubes cannot be used, owing to the difficulty of keeping the solution in them thoroughly mixed; unless the permanganate is

present in excess, there is danger of a deposit of sulphur being formed. A. P.

**Estimation of Potassium Permanganate and of Pyrolusite by Means of Hydrogen Peroxide.** By G. LUNGE (*Ber.*, **18**, 1872—1874).—In the *Chemische Industrie*, 1885, 161, the author proposed to determine the strength of permanganate solution by adding in his nitrometer an excess of hydrogen peroxide to a measured quantity of the solution acidified with sulphuric acid, and measuring the evolved oxygen, half of which is derived from the permanganate. All weighings are thus avoided. Martinon (*Bull. Soc. Chim.*, **43**, 355) states that when acidified permanganate is treated with hydrogen peroxide, manganic peroxide is formed. According to this view, only 3 mols. oxygen would be liberated when 2 mols. permanganate ( $\text{KMnO}_4$ ) are acted on, whereas, according to Lunge's reaction, 5 mols. oxygen should be liberated. In either case, half the oxygen would come from the permanganate and half from the peroxide. The author has repeated his experiments, and finds that under the conditions given by him—where an excess of peroxide is added at once and the evolved oxygen measured—his conclusions are correct. The above method may also be employed for the analysis of pyrolusite, the reaction (in the presence of sulphuric acid) being  $\text{MnO}_2 + \text{H}_2\text{O}_2 = \text{MnO} + \text{H}_2\text{O} + \text{O}_2$ . Of course, as pyrolusite often contains carbonates, the powdered substance must be moistened with sulphuric acid in the decomposing flask before the peroxide is added, or the initial reading of the nitrometer taken.

The author also mentions that the nitrometer may be used for estimating zinc-dust and reduced iron powder by measuring the quantity of hydrogen evolved by the action of an acid. L. T. T.

**Valuation of Manganese Peroxide.** By P. CHARPENTIER (*Compt. rend.*, **101**, 316—318).—The manganese peroxide is heated with hydrochloric acid in a flask connected with a small empty flask, which is kept cool by means of water, and in which any hydrochloric acid condenses, and a second flask containing a solution of pure ferrous sulphate (10 grams per litre) to absorb the chlorine. The last traces of chlorine are expelled from the first two flasks by means of a current of air, and the ferrous sulphate solution is mixed with a small quantity of ammonium chloride and a small quantity of potassium thiocyanate, and a standard solution of potassium hydroxide (1 c.c. = 0.005 Fe) run in until the blood-red colour is discharged.

In the second method, 3.884 grams of the peroxide is distilled with hydrochloric acid in a similar apparatus, and the chlorine absorbed in a litre of water containing 15.18 grams of silver nitrate. At the end of the distillation, the silver solution is mixed with a small quantity of ferric nitrate and titrated with a solution of potassium thiocyanate of such strength that 500 divisions exactly precipitate 15.18 grams of silver nitrate. C. H. B.

**Estimation of the Halogens in Organic Compounds.** By C. ZULKOWSKY (*Monatsh. Chem.*, **6**, 447—454).—The method is a

modification of that described by Zulkowsky and Lepéz (this vol., p. 591). The combustion-tube is of the usual length and is filled in the following way:—First, a few pieces of unplatinised quartzite, then a layer, 45 cm. in length, of 5 per cent. platinised quartzite, and lastly a roll of platinum foil. By using this larger quantity of platinised quartzite, bromine as well as iodine is obtained entirely in the free state.

In the estimation of bromine, about 30 c.c. of an aqueous solution of 2 grams of potassium iodide are put into a small flask fitted with a double-bored cork, through the one hole of which the bent end of the combustion-tube is passed, whilst a tube filled with glass wool, saturated with the potassium iodide solution, is fitted into the other hole: this ensures complete absorption of the gas. The oxygen is passed through an indicator provided with a manometer, in order that the rate at which it is passing into the combustion-tube may be accurately observed. When the combustion is over, the whole apparatus, including the combustion-tube, is washed out with water, and the amount of free iodine in the whole estimated with decinormal solution of sodium thiosulphate.

Chlorine estimations have to be made as previously described (*loc. cit.*), as, even with the greater length of platinised quartzite, most of the chlorine is given off as hydrogen chloride. N. H. M.

**Adulteration of Lemon Oil with Oil of Turpentine.** By G. HERPE (*Arch. Pharm.* [3], 23, 349—350).—The lemon oil is heated in a dry test-tube with a piece of copper butyrate about the size of a pin's head; the temperature is slowly raised to 170°, but must not exceed 180°. If the lemon oil is pure, the copper salt dissolves and colours the oil green. If turpentine oil is present, the oil becomes turbid, is coloured yellow, and reddish-yellow copper protoxide is separated. The difference between the pure and the adulterated oil is very marked, both when warm and after cooling. The test appears very suitable for bergamotte oil and orange-peel oil. J. T.

**Simple Estimation of Sugar in Beet.** By H. PELLET (*Bied. Centr.*, 1885, 428).—10 to 13·024 or 16·20 grams of the mashed roots or sections are placed in a 100 c.c. flask, with long and narrow neck, 50 c.c. water and 2—4 c.c. lead acetate solution are then added, the flask closed with a porcelain ball, and then weighed. Water is added up to the mark, and the whole is heated for 1 hour in a salt water-bath; then, after cooling, the 100 c.c. is made up, and the precipitate filtered off; the figures now read off (?) give the percentage of sugar, if 13·024 grams have been used. E. W. P.

**Estimation of Sugar by Fehling's Solution as conducted at the Municipal Laboratory in Paris.** By C. GIRARD (*Ann. Chim. Phys.* [6], 5, 143—144).

**Behaviour of Tannin with Fehling's Solution.** By A. SONNENSCHN (Dingl. polyt. J., 256, 555).—For the determination of sugar in wine, Fehling's solution is used almost exclusively. As,

however, the results are deficient in accuracy, it was thought that other ingredients present besides grape-sugar might reduce the Fehling's solution. The author, therefore, examined the action of tannin on this solution, and found that it reduces it, 1 gram CuO corresponding with 0.4126 tannin. Glycerol acts in a similar manner. It was found that a number of other substances present in wine reduced Fehling's solution; succinic acid, for instance. The results obtained with this reagent are, therefore, always too high.

D. B.

**Oxalic Acid in Plants.** By BERTHELOT and ANDRÉ (*Compt. rend.*, **101**, 354—360).—The plant is bruised in a mortar, boiled with water for one hour, allowed to macerate for 24 hours, and the liquid decanted off and filtered. The residue is again extracted with warm water, and finally pressed. If it is required to extract the insoluble oxalates the water used for maceration must be mixed with 20—30 c.c. of strong hydrochloric acid for each 100 grams of plant. The mixed filtrates are acidified with hydrochloric acid (if this has not been already added), boiled, and again filtered. The filtrate is made alkaline with ammonia and mixed with an excess of boric acid solution, which in presence of ammonium chloride prevents the precipitation of tartrates, racemates, citrates, &c., or redissolves these precipitates if already formed. The liquid is then strongly acidified with acetic acid, mixed with calcium acetate, heated below the boiling point for about an hour, and the impure calcium oxalate collected and washed. The precipitate is redissolved in hydrochloric acid, reprecipitated by ammonia with subsequent addition of acetic acid, and again collected. This treatment is repeated if necessary, and the purified precipitate is finally weighed as such, converted into calcium sulphate, or treated with a large excess of sulphuric acid and the evolved carbonic oxide measured.

The paper concludes with some determinations of the proportions of soluble and insoluble oxalates in different parts of *Chenopodium quinoa*, *Amarantus caudatus*, *Mesembryanthemum cristallinum*, and *Rumex acetosa*.

C. H. B.

**Estimation of Fat in Palm-nut Meal.** By V. WILM (*Landw. Versuchs-Stat.*, **32**, 1—6).—The author prefers Soxhlet's apparatus to all others, and uses it exclusively. The time occupied in the extraction of the fat from most substances is 3 hours, but it depends on the temperature and the depth to which the flask containing the ether or other solvent is plunged in the water-bath; the time taken to syphon off the ether at different temperatures is, at 60—63°, 6 to 7 minutes; 70°, 3 minutes; 78°, 2½ minutes; 80—82°, 1½ minutes; 85°, 1 minute; but above 80° the process goes on too fast, and there is not time for complete extraction. A cotton-seed cake with a high percentage of fat was extracted in 50 minutes at a temperature of 70—71°. During this time the ether syphoned over 20 times; the percentage of fat was 17.64, and only 0.24 per cent. was left unextracted. In a general way, such a rapid process may not be desirable, but it is useful as a control.

The author's experiments showing the necessity of finely grinding

palm-nuts before extracting the fat have already been quoted (this vol., p. 290). J. F.

**Estimation of Morphine in Opium.** By F. A. FLÜCKIGER (*Arch. Pharm.* [3], **23**, 254—269 and 289—299).—The author discusses the difficulties surrounding the problem, and the various methods which have hitherto been proposed; he also reviews criticisms of the method devised by himself, which is as follows:—8 grams of opium in powder are placed in a closed flask with 80 grams water, the mixture repeatedly shaken during half a day, and the mass then thrown on a folded filter of 125 mm. diameter. Usually 65—68 c.c. of liquid run through. 42.5 grams of the filtrate are taken as containing the morphine from 4 grams of opium, and this amount is placed in a light flask of not more than 100 c.c. capacity; 12 grams (14.7 c.c.) of alcohol of 0.815 sp. gr. at 15°, and 10 grams (13.73 c.c.) of ether are added; the solution still remains clear. Finally, 1 gram (1.04 c.c.) of ammonia of 0.960 sp. gr. is added to the brown mixture, above which, after shaking, a colourless layer of ether forms. The ether is indispensable, as it retains the narcotine in solution which would otherwise remain in the water. The chief advantage of the ether, however, is that the morphine crystallises out from the mixture of alcohol and ether in a pure state. The flask is well stoppered and set aside; after about an hour traces of crystallisation appear, and, with occasional shaking, this is complete in 12 hours, but 12 hours more may be allowed without disadvantage. Two 100 mm. filters are folded and placed in a well-covered funnel; after moistening with ether the ether layer is poured from the flask; 10 c.c. more ether are added to the flask, and then poured on the filter. Finally, the remaining liquid, along with the morphine, is thrown into the filter, and the flask is washed out with about 10 c.c. of the ether-alcohol mixture. The crystals are thrown back into the dry flask, dried at 100°, and weighed as hydrate,  $C_{17}H_{19}NO_3 + H_2O$ , with 5.94 per cent. water.

A sample repeatedly examined by the author and others gave 0.405—0.433 gram morphine for the 42.5 grams solution = 4 grams of the opium. The morphine obtained should always be examined as to its purity. A little is rubbed up with concentrated sulphuric acid and a little bismuth nitrate is strewn over it. If the nitrate contains overmuch nitric acid the morphine becomes red, otherwise brownish-black. Further, the morphine should dissolve completely in a hundred times its weight of lime-water; at the most nothing but a slight flocculent residue should remain. If insoluble crystals are left these are narcotine, and should be quickly filtered and their weight subtracted from that of the morphine. J. T.



## Technical Chemistry.

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**Utilisation of Coal-gas for Heating and Cooking Purposes.** (*Dingl. polyt. J.*, **256**, 534—541.)

**Aseptol.** By E. SERRANT (*Compt. rend.*, **100**, 1544—1547).—The author quotes further experiments to show that aseptol (orthohydroxy-phenylsulphonic acid) is superior to phenol or salicylic acid as an antiseptic. (See this vol., p. 1016.) C. H. B.

**The Employment of Korting's Apparatus for Forcing the Gases through Sulphuric Acid Chambers.** By SCHEURER-KESTNER (*Bull. Soc. Chim.*, **44**, 98—101).—The large amount of resistance which currents of gases in sulphuric acid chambers have to overcome, and which is owing to the friction caused by the Glover's and Gay-Lussac's towers, and the form of pyrites furnaces employed, necessitates the use of an artificial draught; for this purpose Korting's apparatus may be most conveniently and economically employed. When no Glover's tower is used, it is placed at the entrance to the first chamber, and the steam employed is utilised in the manufacture of the acid; inconvenience is sometimes experienced, however, when the apparatus is in this position, owing to the deposition of selenium from the pyrites on the spindle, thus necessitating constant cleaning; it is, therefore, best to have duplicate machines that may be worked turn and turn about during cleaning and repairing operations.

When a Glover's tower is used, the apparatus must be placed beyond the Gay-Lussac tower, as otherwise too much water is introduced into the chambers, and although less economical when used in this position, the apparatus is still quite practicable, and readily regulated. To prevent the corrosion to which the brass or copper of the apparatus is very liable, from the heated acid gases, it may be thinly plated with platinum; an attempt was made to employ porcelain, but it did not stand the heat sufficiently well. A. P.

**Magnesia Industry.** By T. SCHLOESING (*Compt. rend.*, **101**, 131—135).—The magnesium hydroxide obtained from sea-water (Abstr., 1881, 1087 and 1180) can be purified from the sodium chloride which it contains by repeated treatment with fresh water, and can then be used for the manufacture of infusible magnesia bricks. When heated to redness, it loses its water and contracts, and at a white heat it contracts still further, but if kept at this temperature for a short time it undergoes no further change when heated again. The calcined magnesia is very hard, and when ground yields a sandy powder with no tendency to cohere. In order to convert it into bricks, 4 parts by weight or 2 vols. of the magnesia which has been heated at a white heat, are mixed with 1 part by weight, or 1 vol. of magnesia which has been heated only to redness, and the mixture is sub-

jected to a pressure of about 10,000 kilos. per square decimetre. The compressed bricks are then heated for a short time at a white heat in a circulating furnace burning gas or some liquid fuel. If the bricks have been subjected to the pressure given, they undergo very little contraction in the furnace, and do not alter in shape, but if they have not been thus compressed, the contraction is sufficient to destroy the shape of the brick.

C. H. B.

**Progress in Metallurgy.** By MÜLLER and others (*Dingl. polyt. J.*, 256, 506—513).—For the production of the best steel, the steel crucible process is said to be indispensable. At an Austrian steel works the graphite used for the preparation of the crucible consists of—

C.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.
75	13	8	1·8	0·2	2

whilst the clay employed has the following composition :—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	K <sub>2</sub> O.	MgO.	H <sub>2</sub> O.
50·1	33·6	2·8	3·2	0·5	10·1

The crucibles receive a charge of 20 to 30 kilos., and are heated by means of a Siemens furnace. To manufacture hard steel, the heating is continued for five hours, whilst for softer qualities six hours' heating is required. It was found that the steel had absorbed 0·3 per cent. of silicon, and 0·2 per cent. of carbon from the substance of the crucible. Manganese dioxide was reduced by the steel, but at the same time the amount of silicon which was found to migrate from the crucible to the steel was diminished. On introducing furnace gases into the crucible, the carbon only was affected, the silicon and manganese remaining unaltered.

According to L. Schneider the great resistance which tungsten steel offers to atmospheric influences, and the property of yielding a fine damask surface, is due to the presence of tungsten. The hardness of steel is increased by the addition of tungsten, but, unlike carbon, silicon, and phosphorus, it does not form chemical combinations with iron. Hence, in order to manufacture very hard steel, a large addition of tungsten is necessary.

For the purification of copper, W. Braun proposes to pass a current of gaseous hydrogen chloride through the fused metal, whereby all metallic oxides, including the cuprous oxide, are removed as volatile chlorides. A very pure copper of low electrical resistance is obtained. It may be cast free from blowholes in moulds filled with any neutral gas (for instance, carbonic anhydride or coal-gas). The process of poling copper is said to be superseded by this treatment with hydrogen chloride.

According to A. Ledebur the estimation of oxygen in metals and alloys should be effected by ignition in a current of hydrogen. The following percentages of oxygen were found in a number of metals and alloys examined by him :—

Ordinary commercial copper .....	0·227
Copper-plate .....	0·124
Copper fused and cast under a layer of salt .....	0·092
Cast bronze containing 4 per cent. tin from the gun factory of Spandau .....	0·070
Gun-metal containing 10 per cent. tin from the same source .....	0·051
Bell metal from a broken bell, composed of 72·5 per cent. copper, 23·7 per cent. tin, and 1·8 per cent. of lead ....	0·126
Manganese bronze from Spandau, cast with 0·14 per cent. manganese, 1·55 per cent. iron, and 5·86 per cent. tin .....	0·036
Phosphorised bronze from Spandau with 0·004 per cent. phosphorus .....	0·038
Berlin cast brass .....	0·033
Vienna cast brass .....	0·015
Cast nickel, brittle .....	0·304
Malleable nickel (prepared without addition of magnesium)	0·084
Fleitmann's nickel plate (produced with addition of magnesium) from Iserlohn. Malleable .....	0·095
German silver, cast .....	0·061
	D. B.

**Alcoholic Ferments.** By E. C. HANSEN (*Bied. Centr.*, 1885, 417—418).—A ferment has been found in cow-dung and in split ripe fruit, which produces cells like those of *saccharomyces*; in their action they resemble the upper ferment, and form a membrane of mycoderma on the surface of the liquid. Consequently this resembles Bonorden's *Monilia candida*; compared with *Saccharomyces cerevisæ* its action is slow; *monilia* is distinguished from all other ferments by fermenting saccharose without formation of intermediate products.

E. W. P.

**A New Alcoholic Ferment which does not Invert Sugar.** By J. F. TEIXEIRA (*Bied. Centr.*, 1885, 416—417).—Brews made at Busalla were found to be gradually losing their character, and the yeast on examination was found to contain a special ferment, which it was possible to isolate. The cells are globular,  $\frac{1}{3000}$  to  $\frac{1}{5000}$  mm. broad, and do not invert saccharose; possibly this ferment may be used to separate glucose from molasses, for the glucose would be converted into alcohol, whilst saccharose would remain unaltered.

E. W. P.

**Frothy Fermentation.** By M. MÄCKER (*Bied. Cent.*, 1885, 490—492).—In the manufacture of potato spirit, a certain form of fermentation occurs, in which the mash is covered with foam when the temperature reaches 25°; this causes trouble and sometimes loss to the distiller. Delbrück has microscopically examined the yeast which causes it, but finds it healthy; the yield of alcohol from the mash is not reduced; the inconvenience is therefore only mechanical; the author thinks it is due to the employment of unripe potatoes or immature yeast. He suggests certain precautions.

J. F.

**Properties of Malting Barley.** By M. MÄRCKER (*Bied. Centr.*, 1885, 485—487).—Brewers prefer barley which contains the largest amount of starch and the least of proteid bodies; these latter yield extractives which pass into the wort, render the beer turbid, and injure its keeping qualities. Grain which has a fine thin husk is found to yield the largest amount of starch; the seeds should be full and rounded, the percentage of husk in such being smallest.

Some samples examined by the author contained from 19 to 33 grains to the gram; he thinks a fair average would be 25. The best samples showed but 6·5 per cent. of husk; the worst gave 14·2. He thinks 10 per cent. should be expected in average samples. A bright colour indicates soundness; grains damaged by rain are browned at the ends, the barley must also sprout easily; an apparatus for testing that property is in the market.

Brewers, in purchasing, seek for mild, brittle grain, and give the best price for it, whilst hard vitreous corn is neglected. This description is, however, suitable for distillers, as its greater nitrogenous contents afford nutriment to the new yeast. The author finds from numerous experiments that manuring with sodium nitrate increases the percentage of nitrogen in the crop.

J. F.

**Progress in Brewing.** (*Dingl. polyt. J.*, 256, 456—464.)—This paper is an abstract from the Report of the meeting of the Brewery Institute in Berlin.

According to Hayduck the value of hops in their effect on the keeping power of beer is due to a substance which arrests the development of fungoid growth, and depends also on the quantity of tannin contained in the hops, the albuminous matter being coagulated by this constituent. Yeast is not affected by the hops, on the contrary, their presence is beneficial, inasmuch as the yeast is fed by the nutritious matter of the hops. The antiseptic action of different kinds of hops is not, however, the same, although in this respect inferior qualities are as effective as the better kinds, the difference appears to be due to the age, fresh hops giving the best results. There was no perceptible distinction between sulphured and unsulphured hops. Hop extracts were found to be almost useless; this is probably due to the mode of preparation, the active agents undergoing chemical change through excessive concentration. Being unable to separate the bitter principle from the resins, Hayduck considers the latter to be the active antiseptic agents.

Franke, in discussing the question of the quality of barley, laid stress on the exclusive use of stored malt. Noback observed that all stored malt contains more moisture, it forms on grinding a coarser material for the mash, and facilitates thereby the process of cleansing. Reinecke considered the washing of steeped barley an important element in the successful preparation of beer. Gregory reported favourably on the use of Zimmer's wort centrifugal machine, the only fault being the production of much froth.

According to Delbrück, the cause of the reddening of white beer is due to the presence of globular bacteria of the form of sarcina.

In discussing the subject of brewing water, Delbrück quoted cases

in which bad water produced good and bad beer, so that the question of the quality of water is still an open one. The advantage of using hard water was, however, generally admitted. D. B.

**Treatment of Animal Charcoal.** By P. DEGENER and J. LACH (*Dingl. polyt. J.*, 256, 519).—When freshly ignited bone-black is moistened with as much water as it will absorb, and is exposed to air and light, hydrogen peroxide is said to be evolved in noticeable quantity. The purifying power of animal charcoal is increased by this treatment. By substituting alkaline liquids (especially milk of lime) for water, the peroxides of the alkalis and alkaline earths are produced. D. B.

**Lime in the Separation of Beet Juice.** By S. v. EHRENSTEIN (*Bied. Centr.*, 1885, 502).—Four experiments were made in the laboratory on the employment of lime in different forms. One centner of juice was used in each case:—

Per cent. of lime used.	0·5 per cent.	1 per cent.	1·5 per cent.	2 per cent.	2·5 per cent.	3 per cent.
Caustic lime flour	0·14	0·20	0·23	0·30	0·35	0·36
Lime in lumps...	0·15	0·15	0·21	0·26	0·28	0·27
Milk of lime....	0·05	0·09	0·17	0·22	0·22	0·24
Slaked lime in powder .....	—	0·20	0·23	0·27	0·26	0·31

Results as favourable were obtained in large operations; the separation was normal; the presses worked without stoppage, and delivered a hard uniform cake easily ground. J. F.

**Preservation of Milk.** By F. HUEPPE and W. EUGLING (*Bied. Centr.*, 1885, 415—416).—All ferments in milk are destroyed by repeated heating to 65—70°, but it is doubtful whether this method is as practical as that in which the milk is heated to 100° in an atmosphere of steam, although by this last process the taste is affected. By heating to 100°, casein and calcium phosphates are slowly and gradually deposited, but this occurs less if the evaporation is carried to one-third in a vacuum. Analyses of milk preserved without additional sugar are given. E. W. P.

**Lactic Ferment in Milk.** By F. HUEPPE and others (*Bied. Centr.*, 1885, 408—413).—Engling has previously stated his opinion that the lactic fermentation of milk commences immediately on its withdrawal from the udder. Therefore, to ascertain if milk would ferment when removed from all external agents, he arranged that the milk should be drawn into a flask contrived so that any air entering it was filtered through cotton wool; the flask and cotton having been first heated, and the india-rubber connection soaked for two hours in alcohol. In spite of these precautions, the milk fermented at 28—30° in 32 hours. In a second series of experiments, the milking took place in

the open air, snow having fallen, and the flasks were filled some with hydrogen, others with carbonic anhydride. In 52 hours at 28—30°, the milk in the hydrogen flask coagulated, whilst that in the carbonic anhydride flask remained sweet for eight days, but when exposed to the air, coagulation occurred in six hours; the milk contained schizomycetes, as described by Fitz (*Ber.*, 1878, 48). As this bacillus was not noticed in absolutely fresh milk, it is supposed that its spores only were present, and required oxygen for their development. Hueppe considers that the ferments which produce the decomposition of milk originate from the milk glands, and require some small amount of oxygen for development.

Escherich found that milk drawn direct into prepared flasks from healthy women could be kept unaltered at 37° for many weeks; but that milk from women suffering from puerperal fever soon decomposed. Bang states that milk taken from cows suffering from tuberculosis, even if the quarters are healthy, is dangerous, but the danger may be averted by heating to 70°. Such milk is alkaline, poor in fat and sugar, but richer in albuminoids, the ash richer in soda but poorer in calcium phosphates than healthy milk. E. W. P.

**Blue Milk.** By F. HUEPPE and W. EUGLING (*Bied. Centr.*, 1885, 414—415). By using Koch's gelatin method the authors have succeeded in isolating the bacterium which produces blue milk. Whilst on the gelatin plates this ferment is green, but in solutions containing ammonium tartrate it is brown or yellow, and in solution of ammonium lactate it is sky-blue. Milk infected with the cultivated bacillus is alkaline, never acid, and it does not assume the blue colour until acid is present, which may be added or formed by the presence of other ferments. E. W. P.

**Melted Butter.** By W. EUGLING (*Bied. Centr.*, 1885, 484—485). The author says that in certain parts of the Alps it is the custom, during particular seasons, when communication with the markets is difficult, to melt the fine butter over a fire until the water and some of the more easily decomposed albumin is separated, the melted fat keeps better, but the fine aroma is lost. To avoid this he proposes to melt the butter at a low temperature, 45°, and to assist the clarification by adding 2 to 4 grams aluminium sulphate in aqueous solution, and heating for 24 to 36 hours; under such conditions, the fat is clear and preserves its aroma. If the butter be originally rancid, it is partially, sometimes wholly, cured by agitation with lime-water. Good fat prepared thus, when worked with 50 per cent. fresh milk, again yields a butter which possesses nearly the flavour of the freshly churned article. J. F.

**Preparation of Violet Dyes.** (*Dingl. polyt. J.*, 257, 34).—For the manufacture of sulphonic acids of violet colouring matters, *The Farbenfabriken, vormals F. Bayer und Co.*, proceed as follows:—The ordinary commercial methyl-violet is first reduced, and the leuco-base benzylated, then sulphonated and oxidised, or the benzyl violets of commerce are reduced, sulphonated, and the sulphonic acids of the

leuco-base converted into dyes by oxidation. The reduction is effected by means of zinc-dust in acetic acid solution, and the leuco-base is benzylated by treatment with benzyl chloride and sodium hydroxide. The sulphonic acids are obtained by heating the benzylated leuco-bases with sulphuric acid of 66° B., or by treating them with cold fuming sulphuric acid. Mono-, di-, and tri-sulphonic acids are obtained according to the number of benzyl-groups present.

D. B.

**Azo-colours.** (*Dingl. polyt. J.*, 257, 32).—The *Farbenfabriken, vormals F. Bayer und Co.*, have patented a process for the production of soluble combinations of azo-compounds with acid sulphites, and their utilisation in dyeing and printing. For this purpose diazoazobenzene, benzidine, their homologues,  $\alpha$ - and  $\beta$ -diazonaphthalene, or diazobenzenemonosulphonic acid, are combined with  $\alpha$ - and  $\beta$ -naphthol. On treating these compounds in a finely divided state with acid sulphites in hot aqueous or alcoholic solutions, they dissolve in water with a yellow colour. By the action of alkalis or heat, these double compounds are decomposed into their constituents, so that cotton can be dyed or printed with them.

*Dahl und Co.* have found that in preparing a solution of an azo-dye by the action of the diazotised sparingly soluble  $\beta$ -naphthylaminemonosulphonic acids on the  $\alpha$ -naphtholmonosulphonic acids, which correspond with the naphthionic and naphthalidamic acids, an azo-dye separates out, which is derived from the  $\beta$ -naphthylaminemonosulphonic acids I and II, whilst by the addition of salt to the solution the colouring matter from the acid III is deposited.

For the production of yellow dyes the *Farbenfabriken, vormals F. Bayer und Co.*, propose to diazotise benzidine, and combine the solution of tetrazodiphenyl thus obtained with salicylic acid, phenol, or cresol. A yellow colour is produced which dyes cotton in a boiling soap solution without the use of a mordant. Tetrazoditolyl and tetrazodixylyl may be substituted for the tetrazodiphenyl. The tolyl and xylal bases are prepared from nitrotoluene and nitro-xylene by a process analogous to that employed in the manufacture of benzidine from nitrobenzene.

D. B.

**Use of Magnesium for Bengal Lights.** (*Dingl. polyt. J.*, 256, 518).—The *Chemische Fabrik auf Actien*, formerly E. Schering, in Berlin, recommends the following mixtures:—

For white fires	$\left\{ \begin{array}{l} 1 \text{ part shellac} \\ 6 \text{ parts barium nitrate} \\ 2\cdot5 \text{ parts powdered magnesium.} \end{array} \right\}$	fused together and ground.
For red fires	$\left\{ \begin{array}{l} 1 \text{ part shellac} \\ 5 \text{ parts strontium nitrate} \\ 2\cdot5 \text{ parts magnesium powder.} \end{array} \right\}$	fused together and ground.

D. B.

## General and Physical Chemistry.

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**Refractive Indices of the Three Methyl Acrylates.** By G. W. A. KAHLBAUM (*Ber.*, **18**, 2108).—The refractive indices formerly quoted for methyl acrylate and its polymerides (Abstr., 1881, 250) are incorrect through a mistake in calculation. The correct refractive indices for 20° are:—

	H <sub>a</sub> .	N <sub>a</sub> .	H <sub>β</sub> .
Methyl acrylate.....	1.3959	1.3984	1.4045
Liquid polymeride.....	1.4575	1.4600	1.4661
Solid polymeride.....	1.4700	1.4725	1.4786

A. J. G.

**Relationship between Molecular Structure and the Absorption of Light.** By N. KLOBUKOFF (*J. pr. Chem.* [2], **32**, 122—125).

**Chemical Action of Light.** By J. M. EDER (*Monatsh. Chem.*, **6**, 495—505).—When a solution of potassium ferricyanide is decomposed by light, potassium ferrocyanide, soluble Prussian blue, and hydrocyanic acid are formed. The rate of decomposition is increased by the addition of potassium oxalate or citrate, uranic sulphate, or mercuric chloride. Ammonium ferricyanide is more easily decomposed than the potassium salt. A mixture of ferric chloride and potassium ferricyanide decomposes much more rapidly in the presence than in the absence of light.

Sodium nitroprusside is 20 times as sensitive as the ferricyanide. A mixture of nitroprusside and ferric chloride is almost as sensitive as ferric oxalate. Solutions of potassium and ammonium copper oxalates are stable, but sodium copper oxalate blackens on exposure to light, without alteration in weight.

Fehling's solution deposits cuprous oxide on exposure to the light. The addition of ammonium oxalate to sodium sulphindigotate renders the latter sensitive to light. Chlorine-water on exposure to light decomposes from 6 to 12 times as rapidly as bromine-water of the same strength, and is about 1000 times as sensitive as an alcoholic tincture of iodine; tartaric and citric acids increase the rate of decomposition.

A solution of ammonium dichromate in absolute alcohol decomposes more rapidly than a solution in 50 per cent. alcohol.

Mercurous iodide is very sensitive to light. Neither iodine nor hydriodic acid is liberated. According to the author, the following reaction takes place:  $3\text{Hg}_2\text{I}_2 = 2\text{Hg} + \text{Hg}_4\text{I}_6$ . W. C. W.

**Absorption Phenomena of Zircons.** By E. LINNEMANN (*Monatsh. Chem.*, **6**, 531—536).—The author has examined very thin sections of zircons by means of the powerful light produced by an oxyhydrogen flame impinging on a piece of zirconia. Some specimens do not



exhibit any absorption-spectra, others exhibit dark bands identical with the spectra of erbium, didymium, and occasionally of terbium. The Ceylon zircons are richer in erbium than those from North Carolina. The hyacinth zircons from Ceylon do not exhibit sharply defined lines, but broad indistinct bands. The absorption spectrum of the dichroic zircons from Ceylon contains two well-defined lines, namely  $\lambda = 654$  (due to erbium) and  $\lambda = 659$ . The latter is not exhibited by any known element. W. C. W.

**Absorption-spectra of Alkaloids.** By W. N. HARTLEY (*Proc. Roy. Soc.*, **38**, 1—4 and 191—193).—As it is a matter of considerable importance to substitute absolute physical measurements of the alkaloids for uncertain chemical tests and variable physiological results, the author has investigated their absorption-spectra, using diactinic solvents, generally alcohol, and, as a source of illumination, electrodes of alloys of cadmium with either tin or lead. These present the advantage of producing spectra with lines of the same intensity evenly distributed between  $\lambda 4414.5$  and  $\lambda 2145.8$ . The wave-lengths and their reciprocals are given in a series of tables.

The alkaloids are separable into two classes, namely, those which exhibit absorption-bands, such as the active aconitine bases, morphine, codeine, quinine, and their derivatives; and those which transmit continuous spectra, such as inactive aconitine, caffeine, nicotine, atropine, &c. As a general result, it is shown that the absorption-spectra offer a ready means of establishing the identity of the alkaloids and their degree of purity. In comparing spectra of substances of similar constitution, the substitution of an alkyl radicle for hydrogen, and acid radicles for hydroxyl, does not alter the general character of the curve, but may produce variety of length when solutions containing equal weights are examined.

Bases which contain oxidised radicles diminish in diactinic quality in proportion to the amount of oxygen, whilst the apo-derivatives are less diactinic than the parent base, thus indicating an approximate doubling of the molecular weight.

Bases with the pyridine and quinoline nucleus exhibit absorption-bands between  $\lambda 3500$  and  $\lambda 2800$ , those with the benzene nucleus between  $\lambda 2900$  and  $\lambda 2600$ . It thus appears probable that morphine, strychnine, cinchona, and opium bases, are derivatives of pyridine, leucine is a derivative of tetrahydroquinoline, or of a substance of analogous constitution, whilst aconitine, the opium bases, and strychnine give evidence of a benzene nucleus. V. H. V.

**Fluorescence of Rare Earths.** By L. DE BOISBAUDRAN (*Compt. rend.*, **101**, 552—555).—An account of some observations by Crookes and the author on the fluorescence of oxides of the cerite group in different degrees of purity. The fluorescence of hydrochloric acid solutions, with a reversed current, is more intense the higher the proportion of terbium metals and the lower the proportion of yttrium, but the fluorescence of the solid sulphates in a vacuum is more brilliant the lower the proportion of terbium metals, so that the two methods give exactly opposite results.

Some of the oxides showed a power of mutual extinction similar to that recently observed by Crookes in the case of samaria and yttria.

C. H. B.

**Crystalline Reflection in Potassium Chlorate Crystals.** By G. G. STOKES (*Proc. Roy. Soc.*, **38**, 174—185).—It has long been known that crystals of potassium chlorate display a remarkable iridescence. In this paper, the phenomenon is examined in detail, and traced to a reflection from a thin stratum between twin crystals, and is conditioned by the determinate division of the incident wave into two refracted waves accompanied by reflected waves. The thickness of the stratum affects the result through the difference of phase entailed in the two refracted waves on arriving at a second twin plane. The phenomenon of the iridescence of crystals separating from a concentrated solution of the salt differs from that described above, and is shown by the polarisation of light to be a simple case of interference.

V. H. V.

**Charging Secondary Batteries.** By W. H. PREECE (*Proc. Roy. Soc.*, **38**, 348—353).—In this paper an account is given of experiments on the charging of secondary batteries with a view of obtaining efficient and constant currents.

Measurements are adduced of the strength of current flowing through, of the electromotive force, and the density of the liquid; the battery is fully charged when each of these values becomes constant; the evolution of gas-bubbles also affords a ready criterion. An arrangement is also described to prevent electric leakage caused by capillary action, and by the spray of moisture formed by the bursting of the bubbles without the liquid. The capacity of the batteries improves with age; even after long use it appears to be impossible to peroxidise the plate throughout; reversal has a beneficial action by improving the capacity and removes causes of irregular working.

V. H. V.

**Electromotive Force between Metals at High Temperatures.** By T. ANDREWS (*Proc. Roy. Soc.*, **38**, 216—218).—Reversals of electromotive force between platinum and other metals in fused salts have been observed by Hankel, Gladstone, and Tribe. In this paper, there are given quantitative estimations of the electromotive force, and of the extensive deviations from the normal electrochemical positions of platinum with iron or copper in fused salts, such as potassium carbonate and sodium chloride. Thus, taking the case of potassium carbonate with electrodes of platinum and copper, when the salt is fused and resolidified, a reverse electromotive force of 1.037 volts is observed (platinum positive); on remelting the salt and equalising the temperature to 845°, an instant reversal of the direction of the current takes place, the metals resuming their normal position with an electromotive force of 0.88 volt. These interchanges of current direction are almost entirely conditioned by differences of temperature of the salt immediately surrounding the electrodes.

V. H. V.

**Absorption-spectra Thermograms.** By W. W. ABNEY and R. FESTING (*Proc. Roy. Soc.*, **38**, 77—83).—In photographic observations

with the spectroscope, it is often necessary to ascertain the particular media which absorb the blue, but allow the red and infra-red rays to pass. In the latter case it is better to study the relative absorption by means of a thermopile. In this paper observations are recorded with various coloured glasses, solutions of iodine in different menstrua, dyes of different kinds, as well as mixed effects with combinations of these media, the source of radiation being an incandescent lamp. Curves of the absorption-spectra thermograms are given. It is found that the use of cobalt glass is to be avoided, in that it entirely absorbs the infra-red rays at the point of maximum energy; whilst green glass is transparent to rays of very low refrangibility; thus its use for thermometer bulbs, as suggested by the authors, is not advisable. Benzene and alcohol containing iodine in solution show their characteristic absorption-bands, thus introducing complications. Finally, dyes seem only to absorb in the visible spectrum, and have little if any action in the invisible region.

V. H. V.

**Dependence of Boiling Point and Pressure.** By G. W. A. KAHLBAUM (*Ber.*, 18, 2100—2108).—This paper is merely a controversial reply to the criticisms of A. Naumann on the author's deductions regarding the relations between the specific remissions of consecutive members of an homologous series.

V. H. V.

**Boiling Point and Pressure.** By O. SCHUMANN (*Ber.*, 18, 2085—2088).—In a recent pamphlet, Kahlbaum has endeavoured to show that the statical and dynamical methods for the determination of vapour-tensions do not lead to concordant results. In this paper a description is given of an experiment with normal butyric acid by means of an apparatus which permitted of determinations being made by both methods simultaneously; the results were found to be concordant. The discrepancy in the observations probably arises from superheating of the liquid, thus preventing a rapid condensation of the vapour immediately above the surface.

Regarding the specific remission or relative reduction of boiling point to that of pressure, the author has calculated the tangents to the curves, that is, the differential quotients, from the equations to the curves; and has concluded that the tangents decrease with increase of molecular weight under the same conditions of pressure, that is, the curves of the boiling point become greater. For isomeric homologous ethereal salts the tangent differences appear to be constant. The acidic radicle in an ethereal salt influences the course of the curve to a greater degree than the alcoholic radicles.

V. H. V.

**Heat of Combustion of Lauric and Myristic Acids.** By F. STOHMAN and P. RODATZ (*J. pr. Chem.* [2], 32, 93—97).—

	Lauric acid.	Myristic acid.
Heat of combustion per gram..	8738 cal.	9008 cal.
Heat of combustion per gram- molecule.....	1747600 „	2053824 „

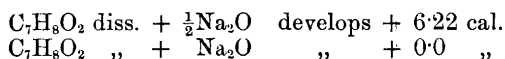
From these and earlier experiments (*J. pr. Chem.* [2], **31**, 297) the authors consider that the heat of combustion of the fatty acids increases by 155039 cal. for every increment of  $\text{CH}_2$ . A. P.

**Specific and Latent Heats of Myristic and Lauric Acids.** By F. STOHMANN and H. WILSING (*J. pr. Chem.* [2], **32**, 80--93).—

	Lauric acid.	Myristic acid.
Specific heat of the solid acid ..	0.457 cal.	0.448 cal.
"    "    liquid acid..	0.5288 "	0.5435 "
"    "    liquid acid }	105.76 "	123.92 "
per gram-molecule..... }		
Heat of fusion of the liquid acid }	43.69 "	47.48 "
per gram..... }		
Heat of fusion of the liquid acid }	8738 "	10825 "
per gram-molecule..... }		

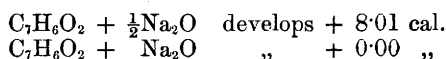
Schüller and Wartha's modification of Bunsen's ice calorimeter (*Pogg. Ann.*, **141**, 1) was used for the determinations. A. P.

**Isomerism in the Benzene Series.** By BERTHELOT (*Compt. rend.*, **101**, 541—546).—*Saligenol*.—Heat of solution at  $18^\circ$  —3.18 cal.

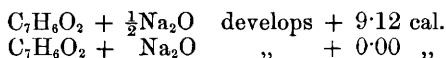


These values correspond with the phenolic function of saligenol, the alcoholic function giving rise to no thermal disturbance in the dilute solutions employed.

*Salicylic Aldehyde*.—Heat of solution almost inappreciable.



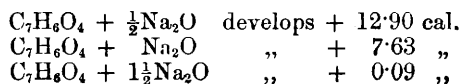
*Parahydroxybenzaldehyde*.—Heat of solution at  $18^\circ$  —4.9 cal.



Both aldehydes behave in the same manner towards alkalis, and exhibit a well-marked phenolic function. When the aldehydes are oxidised to the corresponding acids, the phenolic function disappears in the ortho- but persists in the para-derivative.

Benzaldehyde has no appreciable action on alkalis in dilute solutions. The solubility of compounds of the benzoic series and their congeners does not depend simply on the proportion of oxygen in the compound.

*Protocatechuic Acid*.—Heat of solution  $\text{C}_7\text{H}_6\text{O}_4, \text{H}_2\text{O}$  at  $16.8^\circ$  = —7.32 cal.



This acid behaves as a monobasic acid comparable with acetic acid, and also as a monhydric phenol. This double function exerts an important influence on the action of oxygen on the acid in presence of alkalis. If only one equivalent of base has been added, the solution remains almost colourless; but in presence of two equivalents oxygen is rapidly absorbed and the liquid becomes brown. Similar results are obtained with gallic acid. In all such cases the excess of alkali at once combines with any acid formed by the oxidation, and the heat thus developed promotes the reaction.

*Gallic Acid.*—Heat of solution  $C_7H_6O_5, H_2O$  at  $17^\circ = -7.06$  cal.

$C_7H_6O_5 + \frac{1}{2}Na_2O$	develops	+ 13.12 cal.
$C_7H_6O_5 + Na_2O$	„	+ 7.25 „
$C_7H_6O_5 + 1\frac{1}{2}Na_2O$	„	+ 6.04 „
$C_7H_6O_5 + 2Na_2O$	„	+ 2.65 „
$C_7H_6O_5 + 2\frac{1}{2}Na_2O$	„	+ 1.01 „

Similar values are obtained with potash. Gallic acid behaves as a monobasic acid and a dihydric phenol. The development of heat by further addition of alkali is doubtless due to the fact that excess of alkali diminishes the dissociation of the bibasic phenates. It has been shown in a former paper that pyrogallol behaves as a dihydric phenol, and this agreement between the behaviour of the two compounds is in accordance with their known relations to one another.

*Quinic Acid.*—Heat of solution at  $17.3^\circ = -3.045$  cal.

$C_7H_6O_6 + \frac{1}{2}K_2O$	develops	+ 13.4 cal.
$C_7H_6O_6 + \frac{1}{4}Na_2O$	„	+ 6.54 „
$C_7H_6O_6 + \frac{1}{2}Na_2O$	„	+ 6.69 „
} + 13.23 cal.		

The development of heat is proportional to the amount of alkali added, but the addition of a second and third equivalent of alkali produces no further thermal disturbance, so that quinic acid has no phenolic function.

*Camphoric Acid.*—

$C_{10}H_{16}O_4 + \frac{1}{2}Na_2O$	develops	+ 13.57 cal.
$C_{10}H_{16}O_4 + Na_2O$	„	+ 12.70 „
$C_{10}H_{16}O_4 + 1\frac{1}{2}Na_2O$	„	+ 0.47 „

It is a bibasic acid without any phenolic function.

These results agree with those previously obtained with other compounds belonging to the same series.

C. H. B.

**Thermal Properties of Ethyl Alcohol.** By W. RAMSAY and S. YOUNG (*Proc. Roy. Soc.*, **38**, 329—330).—Substances, as regards the phenomena observable in their vaporisation, can be separated into four distinct classes: (i) those whose vapours are not known to dissociate under the conditions of the experiment; (ii) those which dissociate into homogeneous molecules; (iii) those which gradually dissociate into heterogeneous molecules; and (iv) those which dissociate completely on passage into the gaseous state. As a representative of the first class ethyl alcohol is selected, and measurements have been made

to establish the relation (a) between volume of liquid and temperature at various pressures; (b) between volume of liquid and pressure at various temperatures; (c) between volume of unsaturated and saturated vapour, temperature and pressure; from these data the heats of volatilisation have been calculated.

It is thus shown that the vapour of alcohol in contact with the liquid acquires a density in accordance with the molecular formula  $C_2H_5O$  at about  $50^\circ$ , and that at lower temperatures no molecular condensation is observable. On the other hand, the authors propose to show that the vapour of acetic acid acquires increased density on lowering temperature and pressure, due to the production of complex molecular groups.

The critical point of ethyl alcohol is  $243.6$ ; at a pressure of  $48,900$  mm. the volume of  $3.5$  c.c. is occupied by  $1$  gram of the fluid in its critical condition.

V. H. V.

**Relation of Expansion of Substances in the Gaseous, Vaporous, and Liquid States, to Absolute Temperature.** By C. SCHALL (*Ber.*, **18**, 2063—2067).—According to the molecular theory of gases, the relation of pressure, volume, velocity of molecule, and absolute temperature, is expressible thus:  $\frac{p}{p'} = \frac{v}{v_1} = \frac{u^2}{u'^2} = \frac{T}{T'}$ , supposing

Mariotte's law to be rigidly exact. But gases are far from being ideally perfect, especially near their points of condensation, for the vapours of liquid, when superheated, have a higher coefficient of expansion than perfect gases, and the above relations are expressed by the formula  $\frac{d}{d'} = \frac{v_1}{v} = \left(\frac{T_1}{T}\right)^2$  or  $d' = d \left(\frac{T}{T_1}\right)^2$ . However, this can only

be considered as an approximation, inasmuch as vapours near their liquefaction point quickly decrease in volume up to a certain temperature, and from thence more slowly decrease. In this paper this last point is more particularly illustrated, especially in the case of liquids which dissociate either into heterogeneous or less complex molecules at temperatures slightly above or at their boiling points, such as acetic and formic acids, halogen-derivatives of paraffins, &c.

Again, if perfect gases expand according to the first of the above equations, and superheated vapours according to the second, then the increase of volume of liquids is approximately represented by the formula  $\frac{v}{v_1} = \left(\frac{T}{T_1}\right)^{\frac{1}{3}}$ , which is illustrated in the case of phosphorus trichloride (comp. Mendeléeff, *Trans.*, 1884, 126—135; Thorpe and Rücker, *ibid.*, 135—144).

V. H. V.

**Modification of Petterson and Ekstrand's Method of Vapour-density Determination.** By C. SCHALL (*Ber.*, **18**, 2068—2071).—In this paper a slight modification of Petterson and Ekstrand's method for the determination of vapour-density by Dumas' process is described. The substance to be determined is inclosed within a small tube with capillary neck, which is introduced into a heating apparatus so arranged as to heat any number of such tubes simultaneously.

After heating, the capillary neck is sealed off, and the tube introduced into a volumeter apparatus, and from the weight of the tube when filled and empty, the volume of the flask, and of the air displaced by it in the volumeter, the vapour-density can be calculated. The results obtained with ethyl acetate and carbon tetrachloride are fairly satisfactory.

V. H. V.

**Estimation of Vapour-densities of High Boiling Substances at a Diminished Pressure.** By W. LA COSTE (*Ber.*, 18, 2122—2125).—A modified form of V. Meyer's apparatus with a special apparatus (described with sketch) for collecting the expelled air, is connected with a pump, so that the substance can be volatilised under diminished pressure, the expelled air being afterwards measured at the ordinary pressure. The method is intended for substances which do not boil without decomposition, but may also be used with advantage for high boiling substances which would otherwise require to be heated in a lead-bath. Several examples of vapour-densities determined by this method are given.

N. H. M.

**Relation between Specific Gravity, Capillarity, and Cohesion.** By C. SCHALL (*Ber.*, 18, 2032—2041).—From the equations deduced from the author's previous observations on the relation between capillary attraction and density (this vol., p. 112), it follows firstly, that capillary height increases up to the boiling point of the liquid in proportion to the  $\frac{8}{3}$  power of the sp. gr., and secondly, that the constant of capillarity increases under the same conditions in proportion to the  $\frac{11}{3}$  power. In this paper, the experimental values for  $a^2$ , obtained by Schiff, are compared with those calculated from the equation  $\frac{a^2}{a'^2} = \frac{d^{\frac{8}{3}}}{d'^{\frac{8}{3}}}$  ( $d$  = sp. gr. of liquid at  $0^\circ$ ); these are practically identical. But water appears to be exceptional, and the remainder of the paper contains hypothetical explanations of this phenomenon.

V. H. V.

**Relation between Constants of Capillarity of Members of Homologous Series and their Specific Gravity.** By C. SCHALL (*Ber.*, 18, 2042—2052).

**Motions of Camphor on the Surface of Water.** By C. TOMLINSON (*Chem. News*, 52, 50).—The author explained this and many similar phenomena several years ago. He attributes the motions of camphor on water to the surface tension of the liquid, and hence these motions can always be produced with pure materials and clean apparatus. Camphor rotates on dry mercury, and moves about on water even when supported on a small mica float, which facts set aside any explanations of the phenomenon depending either on disintegration by solution, or on adhesion for water (comp. this vol., p. 951).

D. A. L.

**On Solidification.** By E. REYER (*J. pr. Chem.* [2], 32, 1.0—122).

**Solubility of Salts in Water at Various Temperatures.** By G. A. RAUPENSTRAUCH (*Monatsh. Chem.*, **6**, 563—591).—In determining the solubility of a salt at a given temperature, it is necessary that the flask containing the substance and its solvent should be maintained at a constant temperature and in a state of constant agitation. The author fulfils these conditions by adopting a specially constructed air-bath, and by using a mechanical contrivance for shaking the flask and its contents.

The solubility of the following salts was determined. 100 parts by weight of water dissolve—

<i>t.</i>	NaCl.	CaSO <sub>4</sub> (gypsum).	AgC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .	AgC <sub>3</sub> H <sub>5</sub> O <sub>2</sub> .	AgC <sub>4</sub> H <sub>7</sub> O <sub>2</sub> .	
					Normal.	Iso-.
0	35·571	0·1756	0·7217	0·5118	0·3629	0·7963
10	35·684	0·1922	0·8745	0·6781	0·4189	0·8744
20	35·853	0·2089	1·0371	0·8361	0·4848	0·9608
30	36·079	0·2107	1·2146	0·9934	0·5607	1·0598
40	36·361	0·2115	1·4126	1·1573	0·6466	1·1758
50	36·699	0·2083	1·6365	1·3354	0·7425	1·3132
60	37·091	0·2032	1·8916	1·5352	0·8483	1·4764
70	37·541	0·1960	2·1833	1·7642	0·9641	1·6699
80	38·046	0·1868	2·5171	2·0298	1·1444	1·8980

W. C. W.

**The "Critical Point" in Chemical Decompositions.** By J. H. VAN'T HOFF (*Ber.*, **18**, 2088—2090).—There are many chemical decompositions (dissociations; as for instance, the resolution of ammonium carbamate into carbonic anhydride and ammonia) which show very great analogy to the physical phenomena of evaporation; it therefore seemed probable that the phenomenon of the critical state might also be observed with them. Negative results were obtained in the cases of ammonium carbamate, ammonium hydrosulphide, and phosphonium bromide, but a successful result was obtained with phosphonium chloride in the following manner:—

A mixture of equal volumes of hydrogen phosphide and hydrogen chloride was compressed in a Cailletet's apparatus, until the tube was half filled with phosphonium chloride crystals. The tube was now heated by means of a water-bath. Fusion occurred at 25°, and at 50—51° and a pressure of 80—90° atmospheres, the line of demarcation between liquid and gas disappeared, whilst on cooling, the thick clouding which characterises the critical point was observed.

A. J. G.

**Action of Neutral Salts and of Temperature on the Inversion of Cane-sugar.** By J. SPOHR (*J. pr. Chem.* [2], **32**, 32—55).—The action of neutral salts of the monobasic acids is a simple function of the inversion-constant of the same acid. There is seemingly no distinction between the action of mono- and poly-basic acids. With



the stronger acids the presence of the neutral salts increases, whilst with the weaker acids it decreases the inversion-constant; on the other hand, an increase of temperature diminishes the augmenting action of the neutral salts on the stronger acids, and increases the weakening action of the neutral salts on the weak acids. A. P.

**Chlorine and Bromine Carriers.** By L. MEYER and A. SCHENFELEN (*Ber.*, 18, 2017—2018; compare Page, this vol., p. 36; Willgerodt, *ibid.*, p. 1934).—Ferric and ferrous bromide are very useful bromine carriers for employment in the bromination of organic compounds. As, however, the hydrogen bromide formed frequently acts further on the compounds produced (reducing, for instance, nitro- to amido-compounds), the use of ferric chloride to assist bromination was tried. This acts quite as well as the bromide, and is itself converted into the bromide, whilst hydrogen chloride is evolved. This result seems to show that the metallic salt does not merely exert a contact action, but actually takes part in the reaction. A. J. G.

**Relation of Diameters of Molecules.** By C. SCHALL (*Ber.*, 18, 2052—2062).—In this paper the relations of diameters of molecules of consecutive members of homologous series are considered on the supposition of the cubical or spherical form of the molecules. Then if either of these views were correct, since  $\frac{d}{d'} = \frac{mv'}{m'v}$  then  $\frac{d}{d'} = \frac{mq'^3}{m'q^3}$ , or  $q' = q^3 \sqrt{\frac{dm'}{d'm}}$  ( $d$  = density,  $m$  = mass, and  $q'$  = axis of sphere or side of cube of the molecule). Tables are given to illustrate 1st, the validity of these relations for the vapours of homologous liquids at their boiling points under atmospheric pressure; 2nd, that by the combination of two carbon-atoms or replacement of elements of less by elements of greater atomic weight, the molecular diameters are proportional to the fourth root of the molecular weight, but are increased to the eighth or twelfth root by the introduction of such elements as bromine or iodine. V. H. V.

### Inorganic Chemistry.

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**Pseudo-quadratic Octahedrons of Sulphur.** By C. BRAME  
(*Compt. rend.*, 101, 533—534).

**Valency of Phosphorus.** By A. MICHAELIS and W. LA COSTE  
(*Ber.*, 18, 2118—2122).—The authors point out the evidence for the pentavalent nature of phosphorus offered by two isomeric compounds both capable of existence in the gaseous state and each containing one atom of phosphorus, one atom of oxygen, and three phenyl

groups. Of the three possible formulæ for such a compound, the expression  $\text{PPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  does not agree with the properties of either compound; the nature of the reactions given showing clearly that the newly discovered phenoxydiphenylphosphine (this vol., p. 1214) has the constitution  $\text{Ph}_2\text{P}\cdot\text{OPh}$ , and is unsaturated, whilst triphenylphosphine oxide must be represented by the formula  $\text{O}:\text{PPh}_3$ , in which phosphorus acts as a pentavalent element. A. J. G.

**Solubility of Calcium Sulphate in Saline Solutions.** By W. A. TILDEN and W. A. SHENSTONE (*Proc. Roy. Soc.*, **38**, 331—336).—Although it is generally known that the solubility of calcium sulphate in water attains a maximum at  $35^\circ$ , and is increased by the presence of sodium chloride, yet accurate experiments on these points are still wanting.

In this paper an account is given of determinations of the solubility of calcium sulphate in water, or in solutions of other salts at various temperatures ranging from  $8^\circ$  to  $200^\circ$ . The results show that the solubility of calcium sulphate is increased by the presence of ammonium or sodium chloride, as a probable result of double decomposition, but is diminished by calcium chloride. In each case the form of the curve, representing solubility in terms of temperature, is nearly the same, the solubility being greatly diminished above  $100^\circ$ . On studying the influence of magnesium chloride, it was found that this salt is decomposed and precipitated by the water with rise of temperature, but the solvent action of the hydrochloric acid thus liberated is counteracted by the magnesium chloride remaining in solution, whose action is probably analogous to that of calcium chloride.

V. H. V.

**Formation of Crystallised Magnesium and Cadmium Hydroxides.** By A. DE SCHULTEN (*Compt. rend.*, **101**, 72—73).—12 grams of magnesium chloride,  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ , 340 grams of potash, and 60 c.c. of water, are heated at  $210$ — $220^\circ$  until the magnesium hydroxide completely dissolves. If the proportion of potash is larger, a lower temperature is sufficient. The liquid is allowed to cool, and the solid residue treated with water to remove the alkali. The magnesium hydroxide is left undissolved in the form of small, distinct crystals of sp. gr. 2.36 at  $15^\circ$ ; these dissolve easily in acids and in a warm concentrated solution of ammonium chloride. If soda is used instead of potash, the magnesium hydroxide does not dissolve, but the precipitate rapidly becomes crystalline.

To obtain crystallised cadmium hydroxide, 10 grams of cadmium iodide are dissolved in 150 c.c. of water, mixed with 360 grams of potash containing 13 per cent. of water, and heated until the cadmium hydroxide completely dissolves. When the liquid is cooled the greater part of the cadmium hydroxide separates in white lamellar crystals, with a nacreous lustre. A certain quantity of the hydroxide remains in solution even after the liquid has cooled, and crystallises out after some hours; but if the liquid is diluted with water as soon as it is cold, this portion of the hydroxide separates as a flocculent

precipitate. If soda is used instead of potash the cadmium hydroxide does not crystallise.

Cadmium hydroxide, like magnesium hydroxide, crystallises in flattened hexagonal prisms, easily soluble in dilute acids and in ammonium chloride solution; sp. gr. at  $15^{\circ} = 4.79$ . When gently heated, the crystals lose their water of constitution without changing their form.

C. H. B.

**Atomic Weight of Beryllium.** By T. S. HUMPIDGE (*Proc. Roy. Soc.*, **38**, 188—191).—In this paper determinations of the specific heats of a specimen of beryllium containing 99.2 per cent. of the metal are given at different temperatures up to  $450^{\circ}$ ; the results obtained are in accordance with the empirical formula  $k_t = 0.3756 + 0.00106_t + 0.00000114_t^2$ . The curve representing the relation between specific heat and temperature reaches a maximum at  $400^{\circ}$ , and remains approximately constant between  $400^{\circ}$  and  $500^{\circ}$ ; the number 0.5403 within those limits of temperature when multiplied by 9.1 gives the atomic heat 5.64. Thus beryllium must be classed with carbon, boron, and silicon, as accordant with Dulong and Petit's law at high temperatures. The atomic weight thus deduced is that required by the periodic law, whereas previous determinations between  $10^{\circ}$  and  $100^{\circ}$  gave the atomic weight of 12.6; the conclusion is further confirmed by determinations of the vapour-densities of beryllium chloride and bromide, which accord with the molecular formulæ  $\text{GICl}_2$  and  $\text{GIBr}_2$  respectively.

V. H. V.

**Paratungstates.** By G. v. KNORRE (*Ber.*, **18**, 2362—2366).—Sodium paratungstate, when boiled with water or kept in aqueous solution, is decomposed into normal sodium tungstate and sodium metatungstate. From this it follows that although a freshly prepared solution of the salt is neutral to phenolphthalein and to tropæolin, the least addition of alkalis or acid respectively to the solution sufficing to colour these indicators, yet after boiling or keeping, sufficient soda (about 15 per cent. of the weight of the salt) to convert the metatungstate formed into normal tungstate must be added before phenolphthalein will indicate an alkaline reaction, whilst similarly tropæolin does not indicate an acid reaction until sufficient hydrochloric acid (about 4 per cent.) has been added to convert the normal tungstate formed into metatungstate. This observation also explains the apparent increase in solubility with time noticed by Marignac for sodium paratungstate.

A. J. G.

**Potassium and Sodium Salts of Antimonic Acid.** By G. v. KNORRE and P. OLSCHESKY (*Ber.*, **18**, 2353—2362).—The authors have reinvestigated these salts, especially with a view of ascertaining the nature of the combination in which the water exists. Potassium antimoniate is obtained, in agreement with the older description, as a gummy mass containing a variable quantity of water; when dried at  $100^{\circ}$ , it has the composition  $2\text{KSbO}_3 + 3\text{H}_2\text{O}$ . On further heating to higher temperatures, it gradually loses water, until at  $185^{\circ}$  it contains about 2 mols.  $\text{H}_2\text{O}$ , and at  $350^{\circ}$  still retains more than 1 mol.  $\text{H}_2\text{O}$ ,

which it only loses on ignition; it is therefore impossible to say how much of the water should be regarded as in chemical combination. By the action of carbonic anhydride on an aqueous solution of this salt, a white precipitate is obtained of the formula  $2K_2O, 3Sb_2O_5 + xH_2O$ , thus confirming Heffter's statement (*Ann. Phys. Chem.*, **86**, 418). Dried at  $100^\circ$  this contains 7 mols.  $H_2O$ , which is gradually lost with increase of temperature, until at  $350^\circ$  it only contains 2 mols.  $H_2O$ .

Sodium antimoniate,  $Na_2Sb_2O_6$ , is obtained by adding sodium acetate to potassium antimoniate, by boiling antimonie sulphide with soda, or by the oxidation of antimony salts in presence of hot aqueous soda. If precipitated at the ordinary temperature, it contains 7 mols.  $H_2O$ ; if at  $100^\circ$  then only 6 mols.  $H_2O$ . 1 mol. of water appears to be chemically combined, so that the salt must be regarded as sodium pyrantimoniate,  $Na_2H_2Sb_2O_7$ .

A. J. G.

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## Mineralogical Chemistry.

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**Native Lead and Chromite from the Andaman Islands.** By F. R. MALLET (*Rec. Geol. Surv. Ind.*, **16**, 203—204; *Jahrb. f. Min.*, 1885, **2**, Ref., 5). — At Maulmain, in Burma, cerussite has been found, of a bright red colour, probably due to an admixture of minium. The mineral contains cavities lined with ordinary cerussite, and several of these cavities are partly filled with metallic lead.

At the village of Chuckergaon a great erratic block of chromite was found, resembling a coarsely granular sandstone richly impregnated with iron. At Port Blair, too, chromite is found in workable quantities in serpentine, gabbro, and diorite. B. H. B.

**Analyses of Bituminous Coals from Alabama, Tennessee, and Kentucky.** By N. T. LUPTON (*Chem. News*, **52**, 57—58).

**Rutile and Cassiterite in the Greifenstein Granite.** By M. v. MIKLUCHO-MACLAY (*Jahrb. f. Min.*, 1885, **2**, Mem., 88—90). — The microscopic examination of a specimen of the granite from Greifenstein, near Ehrenfriedersdorf, showed the presence of numerous inclusions in the mica. In order to isolate these inclusions, the constituents of the powdered rock were separated with the help of Thoulet's solution. The heavier portion of the powder was found to consist principally of topaz, with smaller quantities of rutile, cassiterite, tourmaline, and apatite; the lighter portion consisted exclusively of mica with inclusions. On powdering the rock, the heavier inclusions had been separated from the mica, and formed the heavier portion. Some of the crystals, separated under the microscope from the powder, were large enough to be measured; one untransparent red

crystal, 0.68 mm. long and 0.32 mm. broad, proving to be a twin crystal of rutile with the planes  $P, P\infty, \infty P\infty$ . This crystal gave a distinct titanium reaction. The untransparent grains and minute crystals, too small to be measured, gave either a titanium or tin reaction. In order to prove the identity of the inclusions in the mica with the grains and crystals examined, the pure mica richest in inclusions was dissolved in hydrofluoric and sulphuric acids, but both mica and inclusions dissolved. Another portion was then dissolved in hydrochloric and hydrofluoric acids, and in the residue were small topaz crystals and black grains that gave a distinct tin reaction. The author therefore concludes that the  $TiO_2$  and  $SnO_2$ , shown by the analyses, are present in the granite in the form of rutile and cassiterite, and do not belong to the chemical composition of the mica.

B. H. B.

**Rutile from Imfeld.** By F. RINNE (*Jahrb. f. Min.*, 1885, 2, Mem., 20—24).—The author communicates the results of the measurements of the rutile crystals from the dolomite of Imfeld, in the Binnenthal, Wallis. He observed the following 10 planes:— $\infty P, \infty P2, \infty P3, \infty P7, \infty P\infty, P, P\frac{3}{2}, P2, P\frac{5}{2}, P\infty$ . The form  $P\frac{5}{2}$  is a new plane for rutile. In conclusion, he gives a table of the 25 planes hitherto observed on rutile crystals.

B. H. B.

**Russian Caledonite and Linarite.** By P. W. JEREMÉEFF (*Jahrb. f. Min.*, 1885, 2, Ref., 9—10).—Caledonite was found by the author at the Preobraschensk Mine, at Beresowsk. Qualitatively he found  $PbO, CuO, SO_3$ , and  $H_2O$ . The formula of the mineral is  $5PbSO_4 \cdot 2H_2PbO_2 \cdot 3H_2CuO_2$ , according to analyses by Flight of specimens from other localities. The crystalline system is not rhombic, but monoclinic, with an axial system  $a : b : c = 1.0896 : 1 : 1.5773, \beta = 90^\circ 38'$ . The crystals are finely prismatic, elongated in the direction of the axis  $b$ . The forms best developed are:— $\infty P\infty, 0P, \infty P, +2P, -2P$ . Other forms occurring are  $+P, -P, +\frac{2}{3}P, -\frac{2}{3}P, +2P\infty, +\frac{1}{6}P\infty, -\frac{1}{6}P\infty, +\frac{1}{3}P\infty, -\frac{1}{3}P\infty, +\frac{1}{2}P\infty, -\frac{1}{2}P\infty, -\frac{1}{6}P\infty$ . These are, for the most part, the planes observed on crystals from Leadhills, Red Gill, and Rezbanya, but  $+\frac{1}{6}P\infty$  and  $-\frac{1}{3}P\infty$  are new. The crystals are very brittle.  $H. = 2.5$  to 3. The cleavage is basal perfect; less perfect parallel to  $\infty P\infty$ . Colour, bluish-green with greenish-white streak; resinous lustre; transparent; distinctly dichroic. In the Ural, caledonite is not, as is usually the case, associated with linarite, but forms druses in auriferous quartz with cerussite, anglesite, and bismuth ochre.

Linarite was found on auriferous quartz at Beresowsk, in the Ural. It was probably formed as a decomposition-product of aciculite and galena. It is accompanied by cerussite, but not by caledonite. The author has also found it in the Altai Mountains, in the Annensker Mine, with azurite, for which it was formerly mistaken. The Beresowsk crystals show the following forms:— $+P, \infty P\infty, 0P, +\frac{2}{3}P\infty, +P\infty, +\frac{2}{3}P\infty, +2P\infty, -P\infty, \infty P, \infty P2$ . The crystals, 2 to 7 mm. long, are polysynthetic twins, elongated in the direction of the axis  $b$ . The Altai crystals are 3 to 4 mm. long, and tabular. In addition to the

planes exhibited by the Beresowsk crystals, the following planes were observed:  $+\frac{1}{2}P$ ,  $+2P2$ ,  $\frac{1}{2}P\infty$ ,  $P\infty$ ,  $\infty P\infty$ .

From measurements of the angles of crystals from both localities, the monoclinic axial system  $a : b : c = 1.7193 : 1 : 0.8299$ ,  $\beta = 102^\circ 35' 30''$  was calculated. B. H. B.

**Wolfram.** By L. SCHNEIDER (*Dingl. polyt. J.*, 257, 79).—This mineral gave by analysis—

WO <sub>3</sub> .	SnO <sub>2</sub> .	As <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	FeO.
56.70	7.43	traces	3.70	0.035	—	16.07
	MnO.	CuO.	CaO.	MgO.		
	5.63	1.39	4.90	0.36		

D. B.

**Thermo- and Actino-electricity of Rock Crystal.** By W. HANKEL (*Jahrb. f. Min.*, 1885, 2, Ref., 1—2).—A reply to C. Friedel and J. Curie (*Bull. Soc. Min. France*, 5, 282—296). B. H. B.

**The Formation and Alteration of Silicates.** By K. LEMBERG (*Zeit. deutsch. geol. Ges.*, 35, 557—618; *Jahrb. f. Min.*, 1885, 2, Ref., 16—19).—The author has examined a number of silicates with reference to their alteration into zeolite-like compounds. More than 260 analyses are given. B. H. B.

**Milarite.** By F. RENNE (*Jahrb. f. Min.*, 1885, 2, Mem., 1—19).—In 1869 Kennigott described a mineral found in the Val Milar. It was considered to be hexagonal, and was named milarite. In 1877 G. Tschermak found that the mineral was not hexagonal, but that the crystals were a complex group of twin crystals of pseudo-hexagonal character, formed by rhombic individuals. From an optical examination of 30 plates of the mineral cut perpendicularly and parallel to the length of the crystal, the author finds that the mineral was originally hexagonal, but by secondary circumstances the way is prepared for its dissolution into parts of lower symmetry. This dissolution is peculiar to each crystal. The author has no intention of regarding milarite as a typical representative of the hexagonal system. It may be assumed to hold a position on the borders of the rhombic system, secondary causes diminishing its high hexagonal symmetry, so that it then satisfies the demands of the rhombic system. B. H. B.

**The Proportion of Chlorine in Scapolites.** By G. TSCHERMAK (*Jahrb. f. Min.*, 1885, 2, Mem., 72—73).—A reply to Streng (*Jahrb. f. Min.*, 1885, 1, Mem., 182). B. H. B.

**Diagnosis of Zeolites.** By A. LACROIX (*Compt. rend.*, 101, 74—76).—Zeolites which do not form definite crystals can be recognised and classified by means of their optical properties combined with the results of chemical analysis.

Fibrous zeolites can be divided into two groups according to their birefractive power. In one group, which includes pectolite, prehnite,



and thomsonite, the birefractive power approaches that of peridot; in the other, which includes mesotype, stilbite, okenite, laumonite, scolesite, and heulandite, the birefractive power is similar to that of quartz. Zeolites which have no extension are very feebly birefractive.

Fibrous zeolites crystallising in the rhombic system (prehnite, thomsonite, mesotype, okenite) have their extinctions parallel with the edge of extension, and the plane of the axis is parallel with the direction of elongation, except in the case of thomsonite, in which the plane of the axes is transverse. The other fibrous zeolites are monoclinic, and the extinction varies with the species; the plane of the axes cuts the edge of extension at a greater or less angle, but is never perpendicular to it except in heulandite.

In thomsonite, heulandite, and laumonite the sign of extension is sometimes positive, sometimes negative. In pectolite and mesotype it is positive, but negative in prehnite, okenite, scolesite, epistilbite, and some varieties of heulandite.

The bissectrix is positive in pectolite, prehnite, thomsonite, mesotype, okenite, heulandite, christianite, harmatome, and heusterite, but negative in scolesite, laumonite, stilbite, and epistilbite.

Two fibrous zeolites, pectolite and okenite, contain no aluminium; prehnite, laumonite, okenite, stilbite, and heulandite contain calcium; mesotype contains sodium alone; pectolite, thomsonite, scolesite, and epistilbite contain sodium and calcium; christianite contains calcium, potassium, and sometimes sodium; harmatome contains barium; brewsterite barium and strontium.

Amongst the zeolites which show no extension, apophyllite, dolianite, analcime, chabazite, levynite, and gmelinite are uniaxial; eudnaiphite is rhombic; herschelite and gismondite are probably monoclinic.

C. H. B.

**Pseudomorphs of Hornblende after Olivine.** By B. KOLENKO (*Jahrb. f. Min.*, 1885, 2, Mem., 90—91).—Pseudomorphs of hornblende after olivine were first pointed out by F. Becke (Abstr., 1883, 444). The author has observed these pseudomorphs as a very characteristic peculiarity of an interesting variety of greenstone in the Province of Olonez, on the north shore of Lake Onega. Between diorites and diabases, a pale greenish-grey granular rock appears, which, according to the microscopic examination, may be regarded as a highly metamorphosed olivine diabase. In this rock, the olivine is completely pseudomorphed, partly into hornblende and partly into chloritic substance.

B. H. B.

**Unwrought Jadeite from Switzerland.** By A. B. MEYER (*Jahrb. f. Min.*, 1885, 2, Ref., 6—8).—Irregularly shaped specimens of unwrought jadeite of native origin have been found by F. Beck and H. Messikommer on the shores of Lake Neuenburg. Jade and nephrite axes have been frequently found in this district. Analysis gave the following results:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	52·42	26·00	2·02	—	9·05	3·56	7·44	0·20	100·69	3·42
II.	50·30	25·68	2·79	—	11·00	4·45	6·30	0·40	100·92	3·36
III.	57·84	22·08	3·19	0·20	2·51	0·67	14·09	0·38	100·96	3·31

I. Beck's specimen; II. Messikommer's specimen; III. Axe from Lake Neuenberg. The analysis of the axe from the same district should show the identity of the unwrought and wrought material. The author is of opinion that, by chance, an axe, very rich in soda, was employed for analysis, and that others could easily be found containing the same percentage of soda as the unwrought mineral. From these analyses, it is evident that the mineral consists of jadeite, poor in soda, with which some quartz is mixed. The microscopic structure of the unwrought specimens is the same as that of many wrought axes. The author concludes that the specimens are undoubted unwrought jadeite of native origin, and not water-worn axes, nor unwrought material brought from elsewhere.

B. H. B.

**Nephrite from Jordansmühl in Silesia.** By H. TRAUBE (*Jahrb. f. Min.*, 1885, 2, Mem., 91—94).—Kenngott (this vol., p. 1119) has endeavoured to prove that the nephrite from Jordansmühl, described by the author (this vol., p. 361), is not a true nephrite, but probably a mixture of grammatite and diopside. The reasons given are that the Jordansmühl mineral contains, in comparison with other nephrites, too much silica; the low percentage of alumina bears no relation to the percentage of water, and its microscopic structure differs from that of other nephrites. In reply to this, the author now brings forward a number of analyses of unquestionable nephrite from Fischer's work on nephrite. These nephrites agree in their composition with the Jordansmühl nephrite, many of them containing even more silica. Analyses by Fellenberg show, too, that a large percentage of water with a low percentage of alumina is of frequent occurrence. And with reference to the microscopical structure, it has been shown by Arzruni that every occurrence of nephrite may have special peculiarities in its microscopical structure, by means of which nephrites from different localities may be distinguished. The characteristic microscopic needles of hornblende have been shown to be undoubtedly present in the Jordansmühl nephrite.

B. H. B.

**Hypersthene Andesite from Peru.** By F. H. HATCH (*Jahrb. f. Min.*, 1885, 2, Mem., 73—78).—The author gives the results of an examination of the hypersthene andesite collected by Stübel among the volcanoes north of the town of Arequipa. The rock is the lava of the Cirro Chachani. In a ground-mass partly grey and partly brown, porphyritic crystals of felspar occur, with small quantities of hornblende and biotite. An analysis of carefully isolated felspar gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Ignition.	Total.
57·31	27·62	6·06	6·25	3·05	0·25	100·54

The felspar is thus an andesite of normal composition; but apparently mixed with a little orthoclase.  
B. H. B.

**Distribution of Cordierite in Rocks.** By E. HUSSAK (*Jahrb. f. Min.*, 1885, 2, Mem., 81—82).—With reference to the distribution of cordierite in the Hungarian andesites, the author states that the mineral undoubtedly occurs in violet-blue grains, but very rarely, and has decidedly not the enormous distribution that Szabó imagines. The author examined a series of Hungarian andesites with and without garnets, but was quite unable to find any cordierite. In the Hungarian trachytes, under which collective term Szabó includes both the quartz-free and quartzose members of the trachyte and andesite group, cordierite is certainly not so common as quartz. It is frequently difficult to distinguish cordierite from quartz, and Szabó's method of distinguishing cordierite, by the flame test and micro-chemical reaction for sodium, appears unsatisfactory, as there are undoubtedly cordierites containing no sodium. From quartz it is best distinguished by an examination in convergent light, and from felspar by Behrens' micro-reaction for magnesium.  
B. H. B.

**Nickel Ore from Piney Mountain, Oregon.** By W. HOOD (*Jahrb. f. Min.*, 1885, 2, Ref., 15—16).—The ore occurs in two varieties, both amorphous, sp. gr. 2—3; it adheres to the tongue. The first variety does not fall to pieces when placed in water, whilst the second does. Chemically, and in external appearance, the ore resembles garnierite (noumeite); the mode of occurrence, too, is the same. Analysis gave the following results:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> .	NiO.	MgO.	H <sub>2</sub> O.	Sp. gr.
Var. A. ....	48·21	1·38	23·88	19·90	6·63	2·20
Var. B. ....	40·35	1·33	29·66	21·70	7·00	2·20
Garnierite .....	47·23	1·66	24·01	21·66	5·26	2·27
Noumeite .....	47·90	3·00	24·00	12·51	12·73	2·58

Variety A, like noumeite, falls to pieces in water; while variety B, like garnierite, does not fall to pieces.  
B. H. B.

**The Ngawi Meteorite.** By E. H. v. BAUMHAUER (*Jahrb. f. Min.*, 1885, 2, Ref., 30—31).—On the 3rd of October, 1883, between 5 and 5.30 P.M., a meteor was observed in the centre of Java. It moved from west to east, and exploded with a loud report. Stones were found at two points 4½ miles apart, at Gentoeng and at Kedoeng Poetri, both in the district of Ngawi. The meteoric stone of Kedoeng Poetri is in the Leyden Museum. It has a wedge-like form, its weight is 202 grams, and it is covered with a dull, brownish-black crust ½ mm. thick. The sp. gr. is 3·11 at 15°. Under the microscope, the Gentoeng

meteoric stone was found to consist of rounded crystals of olivine, with brown glass inclusions, enstatite occurring almost exclusively in chondra, iron sulphide, and minute particles of iron. The olivine and the numerous chondra were cemented together by the iron sulphide. The stone appears to resemble most closely the meteorites of Warren-ton and Ornans. The results obtained from the mean of three analyses are as follows:—

Nickel-iron .....	3.52	{ Fe..... 2.87	
		{ Ni..... 0.65	
		{ Co..... trace	
Iron sulphide .....	5.71	..... 5.71	
Silicates decomposed by hydro- chloric acid..... }	52.17	{ SiO <sub>2</sub> .... 19.28	
		{ FeO .... 15.61	
		{ NiO .... 1.57	
		{ MnO ... trace	
		{ Al <sub>2</sub> O <sub>3</sub> ... 0.23	
		{ MgO ... 12.42	
		{ CaO .... 1.67	
		{ Na <sub>2</sub> O ... 1.17	
Silicates not decomposed by hy- drochloric acid .....	38.13	{ K <sub>2</sub> O ... 0.22	
		{ SiO <sub>2</sub> .. 23.49	
		{ FeO.... 8.45	
		{ Al <sub>2</sub> O <sub>3</sub> .. 0.55	
		{ MgO .. 2.89	
		{ CaO.... 0.96	
		{ Na <sub>2</sub> O . 1.56	
Chrome-iron .....	0.47	{ K <sub>2</sub> O.... 0.23	
		..... 0.47	
	100.00		100.00
			B. H. B.

## Organic Chemistry.

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**Sodium Fulminate.** By A. EHRENBERG (*J. pr. Chem.* [2], 32, 230—234).—*Sodium fulminate*,  $C_2N_2O_2Na_2 + 2H_2O$ , is obtained by the action of sodium amalgam on an aqueous solution of mercury fulminate; the solution obtained being evaporated over lime and sulphuric acid. It crystallises in colourless, lustrous prisms, which explode with great violence when rubbed; when left for some time over sulphuric acid and lime, the crystals become white and opaque, the anhydrous salt being formed. If the aqueous solution is evaporated on the water-bath, it turns yellow, and finally brownish-red; similar changes occur on exposure to air. When an aqueous solution is electrolysed, the products are ammonium carbonate and cyanate, a brown humus-like substance, carbonic oxide, nitrogen, and nitrous

oxide, and towards the end of the decomposition carbonic anhydride and small quantities of hydrocyanic acid. Hydrogen peroxide converts it into ammonia, sodium carbonate, carbonic anhydride, and hydrocyanic acid.

The *double salt*,  $C_2N_2O_2Na_2, C_2N_2O_2Hg + 4H_2O$ , is obtained by the action on mercury fulminate of half the amount of sodium amalgam necessary for its complete decomposition, or by mixing solutions of the two component salts. It crystallises in colourless plates, is readily soluble in water, and is less explosive than the mercury salt. When a small quantity of dilute acid is added to an aqueous solution, mercury fulminate is precipitated. Strong hydrochloric acid decomposes it, mercury, sodium, and ammonium chlorides, and hydroxylamine hydrochloride being obtained.

A. J. G.

**Fulminuric Acid.** By A. EHRENBURG (*J. pr. Chem.* [2], **32**, 97—111).—On heating silver fulminate with concentrated hydrochloric acid in sealed tubes at  $110^\circ$ , traces of carbonic anhydride and carbonic oxide are given off; one-third of the nitrogen present is obtained in the form of hydroxylamine hydrochloride, and the remaining two-thirds in the form of ammonium chloride. The reaction takes place in a similar manner at  $100^\circ$  under normal pressure, but is complicated by secondary decompositions.

Hydrochloric acid also acts slowly on silver fulminate at the normal temperature, forming a white crystalline substance insoluble in cold water, which leaves no ash on ignition; it contains 4.4 per cent. of H and 22.96 per cent. of C. The nitrogen was not determined. No hydroxylamine or ammonium chloride are formed.

The author considers that the constitution of fulminuric acid is probably in accordance with the formula  $HON : C < \begin{smallmatrix} OC(NH) \\ OC(NH) \end{smallmatrix} >$ .

The oil obtained by Schischkoff by passing hydrogen chloride through alcohol containing potassium fulminate in suspension, is not an ether of fulminuric acid, but has the composition  $C_4H_6EtNO_5$ , and forms additive compounds with ammonia and the amines. The *ammonia compound*,  $C_6H_{14}N_2O_5$ , is obtained on adding alcoholic ammonia to a dry ethereal solution of the oil, in the form of white scales which have a fatty lustre and melt at  $152^\circ$ ; on the addition of acids, the original oil is thrown down unaltered. By heating the ammonia compound a little above its melting point it is decomposed, a fresh compound being formed which has not yet been examined.

The *aniline compound*,  $C_{12}H_{18}N_2O_5$ , crystallises in microscopic, slender, white needles, is soluble in alcohol and ether, and melts at about  $81^\circ$ . The *methylamine* and *ethylamine compounds* are white, crystalline, and deliquescent. By acting on the oil with concentrated nitric acid, oxalic acid, and an oily product which may be distilled with steam are obtained.

A. P.

**Chloro- and Bromo-fulminuric Acids.** By A. EHRENBURG (*J. pr. Chem.* [2], **32**, 111—116).—*Chlorofulminuric acid*,  $C_3H_2ClN_3O_5$ , may be prepared by passing a stream of chlorine through well-cooled dry ether containing silver fulminate in suspension. It forms a brilliant,

white, crystalline mass, readily soluble in ether, chloroform, and alcohol, but insoluble in light petroleum, carbon bisulphide, and benzene; it is decomposed by water. On treating its alcoholic solution with silver nitrate in different proportions, two *silver salts*, (a)  $C_3ClAg_2N_3O_3$ , and (b)  $C_3HClAgN_3O_3$ , are formed. By adding an ammoniacal copper solution to an aqueous solution of the acid, an abundant precipitate of slender, reddish-violet crystals of the *cuprammonium salt* is formed. All salts of this acid are readily decomposed by moisture or heat. An unsuccessful attempt was made to prepare a dichloro-acid, by passing chlorine through ether containing the monochloro-acid in suspension. *Bromofulminuric acid*,  $C_3H_2BrN_3O_3$ , was obtained by gradually adding bromine to ether containing silver fulminurate in suspension; its solubilities are the same as those of the chloro-compound, and it is also decomposed by water, although not so readily; it crystallises in thin white scales, and forms two silver salts similar in constitution to the chloro-derivatives. *Iodofulminuric acid* was also prepared, but has not yet been fully investigated.

A. P.

**Action of Silver Cyanide on Sulphur Chloride.** By R. SCHNEIDER (*J. pr. Chem.* [2], **32**, 187—210).—The products of this reaction are silver chloride and cyanogen sulphide and persulphide. Cyanogen sulphide,  $C_2N_2S$ , has been already described by Linnemann (*Annalen*, **120**, 36).

*Cyanogen persulphide*,  $C_2N_2S_3$ , exists in two modifications, being first obtained as a colourless crystalline mass, soluble in carbon bisulphide, which, after a time, changes spontaneously into an insoluble, probably polymeric, modification; this is an odourless, dark-yellow powder, which becomes strongly electrical when rubbed, and shows signs of crystalline structure under the microscope. It is destitute of taste and odour, and is insoluble in water, alcohol, ether, carbon bisulphide, and chloroform. Concentrated sulphuric acid seems to dissolve it without decomposition, and boiling nitric acid slowly dissolves it with evolution of carbonic anhydride and formation of sulphuric acid. Strong aqueous potash dissolves it and converts it into a substance of acid nature which was not further examined. When heated alone, cyanogen persulphide loses sulphur and carbon bisulphide, and a substance of the formula  $C_3N_4$  is obtained; this forms a dirty yellow or pale yellowish-brown, specifically light powder, which when strongly heated is completely resolved into cyanogen and nitrogen; it thus, both in appearance and properties, closely resembles Liebig's mellon.

A note is appended to the paper stating that Reed finds that the compound of the empirical formula  $C_3N_4$ , when heated with concentrated hydrochloric acid at 170—180°, is converted into cyanuric acid and ammonia, thus confirming the view expressed by Schneider that the substance is *tricyanuramide*,  $N_3(C_3N_3)_3$ .

A. J. G.

**Thiocyanuric Acid.** By A. W. HOFMANN (*Ber.*, **18**, 2196—2207).—Methyl thiocyanurate was already prepared by the author (*Abstr.*, 1880, 797) by heating the thiocyanate at 180—185°. Experiments now show that the reaction does not take place at all when pure

methyl thiocyanate is used, but readily in presence of a few drops of hydrochloric or sulphuric acid. This methyl salt is not acted on by water at 180°; at 220° it gives off a faint odour of mercaptan. Concentrated hydrochloric acid at 100° decomposes it completely into methyl mercaptan and cyanuric acid. The ethyl and amyl salts were prepared in a similar way, and form high boiling liquids which have not been examined.

*Thiocyanuric acid*,  $\text{N}_3\text{C}_3(\text{SH})_3$ , is prepared (1) by heating the methyl salt with sodium sulphide at 250°, and subsequently treating the product with hydrochloric acid; (2) by slightly warming a mixture of cyanuric chloride with sodium sulphide, and adding hydrochloric acid to the solution of the product in water. It is a crystalline substance very sparingly soluble in water, alcohol, ether, benzene, and nitrobenzene; dilute hydrochloric acid has very little action on it at 100°, but decomposes it at 200° into hydrogen sulphide and cyanuric acid. It decomposes sodium carbonate in the cold. *Sodium thiocyanurate*,  $\text{C}_3\text{H}_2\text{NaN}_3\text{S}$ , forms very lustrous crystals, readily soluble in cold water. The *barium salt* (with 2 mols.  $\text{H}_2\text{O}$ ) forms large refractive prisms; it loses all its water at 280°. The *silver, lead, copper, potassium, lithium*, and many other salts were prepared. Alkyl salts are conveniently obtained by the action of cyanuric chloride on the sodiomercaptides of the different alcohols and phenols.

N. H. M.

**Ammelide.** By M. STRIEGLER (*J. pr. Chem.* [2], **32**, 128).—There are two series of basic derivatives of ammelide having the composition  $\text{C}_6\text{N}_8\text{H}_7\text{M}'\text{O}_4$  and  $\text{C}_6\text{N}_8\text{H}_6\text{M}'\text{O}_4$ . The normal ammonium-derivative, a compound of the latter class, forms slender needles; it is very unstable, losing water of crystallisation and ammonia on exposure to the air, the hydrogen ammonium derivative being formed; by heating at 100°, all the ammonia is driven off, pure ammelide remaining. When ammelide is treated with phosphorous pentachloride, cyanuric chloride and phosphorous oxychloride are formed.

A. P.

**Preparation of Additive Products of Hypochlorous Acid.** By R. LAUCH (*Ber.*, **18**, 2287—2289).—The method consists in treating bleaching powder of known strength with excess of boric acid, then adding the theoretical amount of the organic compound, and keeping the mixture in the dark, with constant agitation, until the solution no longer shows bleaching properties. The chlorinated compound is then extracted with ether. Ethyl chlorhydrin was prepared by this method from ethyl ether; chlorobromhydrin from bromallyl; and diallylchlorhydrin from diallyl.

A. P.

**Optical Rotatory Power of Invert Sugar.** By O. GUBBE (*Ber.*, **18**, 2207—2219).—Sulphuric and hydrochloric acids raise the specific rotatory power of invert sugar nearly in proportion to the quantity of acid. For sulphuric acid,  $S = 0$  to 5,  $(\alpha) \frac{20}{D} = - (19.983 + 0.16979 \cdot S)$ . For hydrochloric acid,  $S = 0$  to 3,  $(\alpha) \frac{20}{D} =$



—  $(19.995 + 0.32621 \cdot S)$ ;  $S$  being the quantity of acid calculated in the proportion 10 sugar to 100 water. Oxalic acid has no influence. The influence of water and of temperature were also examined; tables are given showing the results of the experiments.

N. H. M.

**Action of Bromine on Dimethylamine.** By F. RASCHIG (*Ber.*, 18, 2249—2251).—On the addition of bromine-water to a solution of dimethylamine, dimethylamine hydrobromide and hypobromite appear to be formed, and these, by the action of a further amount of bromine, yield a voluminous yellow precipitate of a substance of the formula  $C_2H_5Br_3NO_2$ . This compound volatilises at the ordinary temperature, and is decomposed at  $60^\circ$ , bromine-vapour being given off; it is dissolved by hydrochloric acid, being converted into dimethylamine hydrochloride. The tribromo-derivative is very unstable, being readily decomposed by acids or alkalis; it is soluble in ether and alcohol, but is insoluble in water.

A. P.

**Action of Ethyloxalic Chloride on Derivatives of Carbamide and Guanidine.** By M. STOJENTIN (*J. pr. Chem.* [2], 32, 1—32).—*Thiocarbanilidothioxanilide*,  $NHPh \cdot CS \cdot CO \cdot NPh \cdot CS \cdot NHPh$ , is prepared by gradually adding ethyloxalic chloride to a warm solution of diphenylthiocarbamide in benzene until ethyl chloride and carbonic anhydride are no longer given off. The substance crystallises in yellow, hair-like needles, soluble in ether, concentrated sulphuric acid, and in aniline; dilute alkalis also dissolve it, but with partial decomposition. It is insoluble in, and partially decomposed by, water, melts at  $231^\circ$ , and is decomposed by keeping for any length of time, hydrogen sulphide being formed. When heated at  $200^\circ$  in a sealed tube with fuming hydriodic acid, it is completely decomposed. When treated with fuming nitric acid, the compound  $C_{15}H_5N_4SO_5$  is formed as a yellowish-white crystalline precipitate; it is insoluble in ether, &c., and is sparingly soluble in water and boiling alcohol; it has a slightly alkaline reaction, and melts at  $235^\circ$ ; when warmed with dilute soda, paranitraniline is formed, and also a white crystalline compound which has not yet been examined.

On dissolving thiocarbanilidothioxanilide in boiling alcohol and gradually adding an alcoholic solution of silver nitrate, diphenylparabanic acid is formed, and by dissolving this compound in warm fuming nitric acid and pouring the solution so obtained into cold water, a precipitate of *dinitrodiphenylparabanic acid*,  $C_{15}H_5N_4O_7$ , is thrown down in small white prismatic needles; it is insoluble in the usual solvents, and yields nitraniline when heated with aqueous alkalis. Thiocarbanilidothioxanilide, when treated with aniline and silver nitrate, yields oxalyltriphenylguanidine. By treating dry thiocarbanilidothioxanilide with alcoholic ammonia, a white crystalline substance having the composition  $C_{14}H_{15}N_4O_3$  is formed; it is tasteless; ordinary nitric acid has no action on it, but the fuming acid dissolves it at a gentle heat, and on pouring the solution into water a yellow crystalline compound is precipitated having the composition  $C_{13}H_{14}N_5O_6$ ; it melts at  $235^\circ$ , and when boiled with aqueous alkalis is decomposed, ammonia and nitraniline being formed. A second

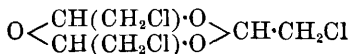
substance is formed by the action of alcoholic ammonia on thio-carbanilidothioxanilide, and separates from the mother-liquors in slender, pearly scales, readily soluble in ether and alcohol; it contains sulphur, and has an extremely bitter taste; it melts at 130°.

*Oxallyldiphenyldithiobiuret*,  $\begin{smallmatrix} \text{CO}\cdot\text{NPh}\cdot\text{CS} \\ \text{CO}\cdot\text{NPh}\cdot\text{CS} \end{smallmatrix} \text{NH}$ , is obtained by acting on monophenylthiocarbamide with ethyloxalic chloride; it crystallises in hair-like needles, melts at about 215°, and dissolves in aqueous soda with a yellow colour, giving off a characteristic fragrant odour; when treated with silver nitrate, a white crystalline compound is formed. On warming monophenylcarbamide with ethyloxalic chloride, carbonic oxide and ethyl chloride are given off, and two new compounds are formed, *ethylic phenylallophanate*,  $\text{NPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{COOEt}$ , which forms white needles and melts at 120°, and *monophenylparabanic acid*,  $\begin{smallmatrix} \text{CO}\cdot\text{NPh} \\ \text{CO}\text{—NH} \end{smallmatrix} \text{CO}$ , which crystallises in silky scales, is readily soluble in alcohol, ether, and hot water, and melts at 208°; it has a slightly acid reaction, and is soluble in hydrochloric acid without decomposition.

*Diphenylparabanic acid*,  $\begin{smallmatrix} \text{CO}\cdot\text{NPh} \\ \text{CO}\cdot\text{NPh} \end{smallmatrix} \text{CO}$ , may be obtained by gradually adding ethyloxalic chloride to benzene containing diphenylcarbamide in suspension; it forms white, glistening needles, melts at 204°, dissolves readily in alcohol or ether, and is insoluble in water; by heating with alkalis, aniline and oxalic acid are formed.

*Carbonyltriphenylguanidine hydrochloride*,  $\text{CO} \begin{smallmatrix} \text{NPh} \\ \text{NPh} \end{smallmatrix} \text{C} : \text{NPh}, \text{HCl}$ , is formed by the gradual addition of ethyloxalic chloride to benzene containing triphenylguanidine in suspension; it forms white needles, melts at 190°, and is slowly decomposed on keeping; when reduced with sodium amalgam or alcoholic potash, triphenylguanidine is again formed, and by the action of silver nitrate *carbonyltriphenylguanidine nitrate*,  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_4$ , is obtained; it crystallises in octahedra, dissolves in alcohol, but is insoluble in water; it melts at 185°; on heating it with hydrochloric acid in sealed tubes at 160°, a substance crystallising in beautiful, long, reddish needles is formed, but this has not yet been further examined. On treating carbonyltriphenylguanidine with nitric acid, a substance having the composition  $\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2 + \frac{1}{2}\text{H}_2\text{O}$  is obtained in slender white needles; it melts at 200°, and appears to be identical with a substance formed in small quantities together with carbonyltriphenylguanidine nitrate by the action of silver nitrate on carbonyltriphenylguanidine. A. P. ...

**Parachloraldehyde.** By K. NATTERER (*Monatsh. Chem.*, **6**, 519—523).—The author confirms the accuracy of his statement (Abstr., 1882, 1045) that parachloraldehyde can be volatilised in a vacuum without dissociation. The density of the vapour at 181.5°, and under a pressure of 46.9 mm., is 8.25 referred to air as unity. The constitutional formula of the compound will be



This compound is not attacked by nascent hydrogen evolved from iron and acetic acid, by silver acetate, or alcoholic ammonia at 100°, or by boiling with potassium hydroxide. W. C. W.

**Oxidation of the Ketones.** By G. WAGNER (*Ber.*, **18**, 2266—2269).—By heating methyl butyl ketone with chromic mixture in sealed tubes at 150—155° for five hours, butyric and normal valeric acids are formed, whilst on conducting the oxidation at the ordinary temperature, butyric acid alone is produced; this confirms the author's theory that the oxidation products of the ketones vary with the pressure, temperature, &c. (*J. Russ. Chem. Soc.*, 1884 (1), 645 and 695.) A. P.

**Reactions with Nitromethane.** By A. PFUNGST (*J. pr. Chem.* [2], 237—238).—*Glyceryl formate dichloride*,  $C_3H_5Cl_2 \cdot O \cdot CHO$ , is obtained by heating dichlorhydrin (1 mol.) with nitromethane for 20 hours at 220°; it is a colourless oil of ethereal odour, and yields monoformin when warmed with alcoholic soda.

Ethylene chlorhydrin and nitromethane yield a colourless chlorinated oil, boiling at above 130°; it is still under investigation.

Nitromethane does not act on phenylhydrazine up to 20° otherwise than as a solvent. If a mixture of the two is heated for 10 hours at 140°, methylamine and a crystalline substance are obtained, the latter in quantity too small for further investigation. A. J. G.

**Fat of the Fruit of *Myristica Surinamensis*.** By C. L. REIMER and W. WILL (*Ber.*, **18**, 2011—2017).—The fruits of this plant have recently been imported into Germany under the name of oil nuts. The fruit is about the size of a cherry, the shell is dark-grey, ribbed, and very easily broken. The kernel is brown and hard and shows a white and brown marbled surface when cut across. The powdered kernels yield 73 per cent. of their weight to boiling ether. The crude fat left on evaporation of the ether forms a hard brittle mass of yellowish-brown colour and crystalline structure and melts at 45°. The main constituent of this fat is trimyristin, free myristic acid also occurs in small quantity, together with various amorphous substances which were not further investigated.

Trimyristin (like tripalmitin and tristearin) appears to occur in two modifications having different melting points. If it is heated to 55° it melts, and when allowed to cool forms a crystalline mass still showing the same melting point. If, however, the fused mass is heated to 57—58° and then allowed to cool, it solidifies to a transparent porcelain-like mass which melts at 49°. When this last modification is heated at 50° for half a minute, it becomes again solid and crystalline, and now shows the melting point 55°.

Ethyl myristate boils at 295°. When myristamide is heated with brominated potash, it is converted into the mixed carbamide,  $C_{13}H_{27} \cdot NH \cdot CO \cdot NH \cdot C_{14}H_{27}O$ . This crystallises well, melts at 103°, is insoluble in water, nearly insoluble in cold alcohol, soluble in ether, and when fused with potash gives a good yield of the amine of the next lower series. A. J. G.

**Iodopropargylic Acid.** By B. HOMOLKA and F. STOLZ (*Ber.*, **18**, 2282—2286).—*Potassium iodopropargylate*,  $\text{CI}:\text{C}\cdot\text{COOK}$ , crystallises in small lustrous needles and is very hygroscopic. The *barium salt*,  $(\text{CI}:\text{C}\cdot\text{COO})_2\text{Ba}$ , forms an amorphous mass, readily soluble in water. The *copper salt*,  $(\text{CI}:\text{C}\cdot\text{COO})_2\text{Cu}$ , and *silver salt*,  $\text{CI}:\text{C}\cdot\text{COOAg}$ , are also described. An attempt made to obtain iodopropargylic acid by the action of an aqueous potassium iodide solution of iodine on cupric propargylate proved unsuccessful, *tetraiodoethylene*,  $\text{CI}_2:\text{CI}_2$ , being formed; this crystallises in prisms, and melts with decomposition at about  $165^\circ$ , it is also formed by the action of an aqueous potassium iodide solution of iodine on the copper compound of acetylene.

*Bromiodacrylic acid*,  $\text{C}_2\text{HIBr}\cdot\text{COOH}$ , is obtained by dissolving iodopropargylic acid in fuming hydrobromic acid; it forms colourless needles, melts at  $96^\circ$ , and is soluble in ether, alcohol, and hot water; it is not identical with the isomeric acid obtained by Hill (*Abstr.*, 1879, 616).

*$\beta$ -Diiodacrylic acid*,  $\text{C}_2\text{I}:\text{CH}\cdot\text{COOH}$ , obtained by dissolving iodopropargylic acid in fuming hydriodic acid, forms yellowish prisms, melts at  $133^\circ$ , and is soluble in alcohol, ether, and hot water.

*$\alpha$ - $\beta$ -Diiodacrylic acid*,  $\text{CHI}:\text{CI}\cdot\text{COOH}$ , is formed by boiling an ethereal solution of propargylic acid with a slight excess of iodine; it crystallises in very fine, prismatic needles, melts at  $106^\circ$ , and is soluble in ether, alcohol, and hot water; it volatilises with steam.

*Dibromiodacrylic acid*,  $\text{CIBr}:\text{CBr}\cdot\text{COOH}$ , which is possibly identical with the compound obtained by Mabery and Lloyd (*Abstr.*, 1882, 1048), may be prepared by adding excess of a solution of bromine in chloroform to a well-cooled solution of iodopropargylic acid in chloroform; it forms magnificent, silky needles, and melts at  $147^\circ$ ; it is soluble in alcohol, ether, and hot water.

*Dibromiodethylene*,  $\text{CIBr}:\text{CBrH}$ , is obtained on adding bromine to an aqueous solution of iodopropargylic acid; it forms small, yellowish prisms and melts at  $66^\circ$ .

*Triiodacrylic acid*,  $\text{CI}_2:\text{CI}\cdot\text{COOH}$ , may be obtained by heating an ethereal solution of iodopropargylic acid with the theoretical amount of iodine in a reflux apparatus for two hours; it forms large, colourless prisms, which turn reddish on exposure to light; it melts at  $207^\circ$ , and is soluble in ether, alcohol, and hot water.

*Diiodobromacrylic acid*,  $\text{CI}_2:\text{CBr}\cdot\text{COOH}$ , is obtained by heating an ethereal solution of iodopropargylic acid with the theoretical amount of bromine iodide for some hours in a reflux apparatus; it forms colourless lustrous scales, and melts at  $182^\circ$ . It is isomeric with that obtained by Mabery and Lloyd (*Abstr.*, 1881, 1125).

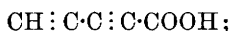
A. P.

**Polyacetylene Compounds.** By A. BAEYER (*Ber.*, **18**, 2269—2281).—A better yield of diacetylenedicarboxylic acid (this vol., p. 759) is obtained if free propargylic acid is employed for its preparation instead of the ethyl salt.

*Ethyl diacetylenedicarboxylate*,  $\text{C}_{10}\text{H}_{10}\text{O}_4$ , may be prepared by passing hydrogen chloride through an alcoholic solution of diacetylenedicarboxylic acid cooled to  $0^\circ$ ; it is a fragrant smelling oil, and boils at

184° under 200 mm. pressure; by reducing its alcoholic solution with zinc-dust and hydrochloric acid, propargyl ethyl ether is formed.

The acid obtained by boiling an aqueous acid salt of diacetylenedicarboxylic acid (*loc. cit.*) is *diacetylenemonocarboxylic acid*,



it is very sensitive to light. The alkaline copper compound yields on oxidation with potassium ferrocyanide *tetracetylenedicarboxylic acid*,  $\text{COOH}\cdot\text{C}:\text{C}:\text{C}:\text{C}:\text{C}:\text{C}:\text{C}\cdot\text{COOH}$ ; this forms fine colourless needles, which blacken quickly even when protected from light; it is extremely explosive, and yields sebacic acid when reduced.

By warming ammonium diacetylenedicarboxylate with cuprous chloride at 30°, a reddish-violet precipitate of the copper compound of diacetylene is formed, and this, when heated with a concentrated solution of potassium cyanide, yields a gas which has an odour somewhat like dipropargyl, and which when passed through an ammoniacal solution of cuprous chloride again yields the reddish-violet precipitate; with an ammoniacal silver solution, it forms a yellow precipitate which is exceedingly explosive; exploding even when rubbed in the wet state between the fingers.

*Ethyl iodopropargylate*,  $\text{CI}:\text{CCOOEt}$ , may be prepared by acting on the wet copper compound of ethyl propargylate with a solution of iodine in aqueous potassium iodide; it crystallises in large colourless prisms, and melts at 68°. The *free acid*,  $\text{CI}:\text{C}\cdot\text{COOH}$ , may be obtained by saponifying the ethyl salt; it forms slender colourless prisms and melts at 140°.

*Moniodoacetylene*,  $\text{CI}:\text{CH}$ , may be prepared by passing steam through an aqueous solution of barium iodopropargylate; it distils in oily drops which solidify at a lower temperature, and has a disagreeable odour somewhat like phosphorus oxychloride. It is soluble in water, and is very volatile; its vapour appears to be exceedingly poisonous; on keeping for some time it changes into an odourless crystalline compound, which melts at 171° and is probably triiodobenzene. With ammoniacal cuprous chloride, moniodoacetylene forms a purple-red precipitate, which soon changes into a mixture of cuprous iodide and the red copper acetylene compound.

*Diiodoacetylene*,  $\text{CI}:\text{CI}$ , probably identical with the compound obtained by Berend (*Annalen*, **135**, 256), melts at 78°; if rapidly heated it explodes slightly, and by heating for some time at 100° it is decomposed, a solid substance melting at 184° being formed, which is probably hexaiodobenzene.

*Diiododiacetylene*,  $\text{CI}:\text{C}\cdot\text{C}:\text{CI}$ , is obtained by treating the silver diacetylene compound under water with a solution of iodine in aqueous potassium iodide; it forms colourless crystals and melts at 101°; it smells like iodoform, and when heated in tubes explodes violently with a flash of red light; if kept for some time exposed to light it is polymerised, forming a brown crystalline mass which detonates on heating. The author discusses at some length the constitution of acetylene compounds, explaining the reactions by a slight modification of the Le Bel and Van't Hoff theory.

A. P.

**Action of Sulphur Chloride on Ethyl Sodacetoacetate.** By K. BUCKKA (*Ber.*, **18**, 2090—2093).—The formation of hydroxy-uvitic acid by the action of chloroform on ethyl sodacetoacetate (Oppenheim and Pfaff, this Journal, 1874, 1161) suggested the possibility that by substituting sulphur chloride for chloroform a substance related to the thiophen-group might be formed. It was found, however, that the product of the reaction was a compound of the formula  $S(CH_3\bar{A}c:COOEt)_2$ , a sulphide of ethyl acetoacetate. This crystallises in colourless prismatic needles, and melts at 80—81°. Many attempts were made to obtain a condensation-product from this by the action of reducing agents, but they were all unsuccessful, owing to the readiness with which the sulphur is eliminated. The action of sulphur chloride on derivatives of ethyl acetoacetate and on ethyl sodomalonate is being investigated.

Carbonyl chloride acts on ethyl sodacetoacetate with formation of ethyl chloracetoacetate, carbonic oxide, and sodium chloride.

A. J. G.

**Conversion of Ketonic Acids into Unsaturated Lactones.** By L. T. THORNE (*Ber.*, **18**, 2263—2264).—By the distillation of  $\alpha$ -methyl- $\beta$ -acetopropionic and  $\alpha$ -ethyl- $\beta$ -methylacetopropionic acids, water is separated, and the unsaturated lactones,  $C_6H_8O_2$  and  $C_8H_{12}O_2$ , are formed. These compounds and the substance  $C_7H_{10}O_2$ , previously obtained from  $\alpha$ -ethyl- $\beta$ -acetopropionic acid (*Trans.*, 1881, 343), are all analogous to  $\beta$ -angelica lactone lately described by Wolff (this vol., p. 1123), but are more stable, as the isomeric derivatives corresponding with Wolff's  $\alpha$ -angelica lactone appear to be formed with much greater difficulty, and none have as yet been isolated. It therefore appears that the introduction of radicles of the fatty series into this class of lactones increases their stability.

A. P.

**Symmetrical and Unsymmetrical Dimethylsuccinic Acids.** By R. LEUCKART (*Ber.*, **18**, 2344—2352).—Otto and Beckurts have stated (this vol., p. 754) that symmetrical dimethylsuccinic acid (m. p. 193°), prepared from pyrocinchonic acid, yields an anhydride, from which by the action of water they obtained unsymmetrical dimethylsuccinic acid (m. p. 240—241°). The author finds that the symmetrical dimethylsuccinic acid prepared from ethyl  $\alpha$ -bromopropionate and ethyl sodomethylmalonate (Bischoff and Rach, this vol., p. 885), when heated, yields an anhydride,  $C_6H_8O_3$ , crystallising in iridescent plates, and melting at 79—81°. This, however, seems to be a mixture, as when dissolved in water it gives in addition to *symmetrical* dimethylsuccinic acid, a small quantity of an acid crystallising in lustrous prisms, and melting at 121—122°. If, therefore, Otto and Beckurts' acid is converted into an isomeric of higher melting point by heating and dissolving in water, it cannot be identical with dimethylsuccinic acid, although agreeing with it in physical properties.

Unsymmetrical dimethylsuccinic acid,  $COOH \cdot CH_2 \cdot CMe_2 \cdot COOH$ , can be synthesised by boiling ethyl isobutenyltricarboxylate with hydrochloric acid. The acid so obtained melts at 138—139°, and is identical with that obtained by Pinner by the oxidation of mesitylenic

acid (Abstr., 1882, 942), and probably also with that obtained by Kachler from phorone (this Journal, 1872, 1011). *Ethyl isobutenyl-tricarboxylate*,  $\text{COOEt} \cdot \text{CMe}_2 \cdot \text{CH}(\text{COOEt})_2$ , obtained by the action of ethyl  $\alpha$ -bromoisobutyrate on ethyl sodomalonate, is a liquid boiling at  $181\text{--}185^\circ$  under 30 to 40 mm. pressure, and at  $279\text{--}281^\circ$  with slight decomposition under the atmospheric pressure. A. J. G.

**Glycide Pyroracemate.** By F. ERHART (*Monatsh. Chem.*, **6**, 511—518).—When a mixture of equivalent quantities of glycerol and glyceric acid is heated in a retort at  $120^\circ$ , carbonic anhydride and acraldehyde are given off, and an acid aqueous distillate passes over. When the temperature rises to  $190\text{--}240^\circ$ , *glycide pyroracemate* distills over, and solidifies in the receiver. On recrystallisation, this compound is obtained in long, colourless needles. It melts at  $82^\circ$ , and boils at  $240^\circ$  without decomposition. It is soluble in alcohol and in hot water. The pyroracemate unites with metallic oxides to form crystalline compounds.  $\text{C}_6\text{H}_5\text{KO}$ , crystallises in silky needles which dissolve freely in water. The calcium salt,  $(\text{C}_6\text{H}_5\text{O}_4)_2 \cdot \text{Ca}(\text{OH})_2 + 2\text{H}_2\text{O}$ , is efflorescent. The copper compound,  $(\text{C}_6\text{H}_5\text{O}_4)_2 \cdot \text{Cu}(\text{OH})_2 + 3\text{H}_2\text{O}$ , is sparingly soluble in cold water.

The author points out that glycide pyroracemate is identical with Schlagdenhauffen's "pyruvine" (this Journal, 1872, 1000), and also with Böttinger's so-called glycurvic acid (this Journal, 1877, ii, 443), and further that "glycurvic" acid is not formed by the distillation of pure glyceric acid. It is only produced when the glyceric acid contains glycerol. W. C. W.

**Malic Acid.** By H. VAN'T HOFF, jun. (*Ber.*, **18**, 2170—2172).—Malic acid, prepared from the lævo- and dextro-acids, and that obtained by the action of soda on fumaric acid, are shown by crystallographic measurements to be identical with one another and with Pasteur's acid (see also this vol., p. 1049). N. H. M.

**Substitution-products of Acetonedicarboxylic Acid.** By M. DUNSCHMANN and H. v. PECHMANN (*Ber.*, **18**, 2289—2290).—By treating acetonedicarboxylic acid with hydrogen cyanide and saponifying the nitrile thus produced, citric acid is again formed (compare this vol., p. 138). Like ethyl malonate and ethyl acetoacetate, ethyl acetonedicarboxylate forms metallic substitution-compounds with alkali-metals and copper, and these may be again replaced by organic radicles. Substitution-products of acetonedicarboxylic acid were formed by a method similar to that used for the preparation of substituted acetoacetates, from one to four organic radicles being introduced into the  $\text{CH}_2$  groups. The substitution-products thus obtained were partly liquid and partly crystalline. No unsymmetrical compounds were observed, but those containing an uneven number of substituted radicles were much less stable than those containing an even number. By the saponification of these compounds, carbonic anhydride is given off, and the corresponding ketone obtained. No details are given. A. P.

**Action of Ammonia on Ethyl Acetonedicarboxylate.** By H. v. PECHMANN and H. STOKES (*Ber.*, **18**, 2290—2292).—*Ethyl β-hydroxyamidoglutamate*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{NH}_2)\cdot\text{CH}_2\cdot\text{COOEt}$ , is prepared by acting on ethyl acetonedicarboxylate with aqueous ammonia. It forms colourless needles, melts at  $86^\circ$ , and is decomposed by acids, ammonia being given off. Alkalis convert it into the compound  $\text{C}_5\text{N}_2\text{H}_6\text{O}_2$ , which the authors propose to call glutazin. This forms colourless needles, which are decomposed at a high temperature without melting. On treatment with bromine-water, *pentabromacetetylacetamide*,  $\text{CBr}_3\cdot\text{CO}\cdot\text{CBr}_2\cdot\text{CONH}_2$ , is formed. By the action of phosphorous pentachloride on glutazin, four new chloro-compounds are formed,  $\text{C}_5\text{N}_2\text{H}_4\text{Cl}_2\text{O}_2$ , melting at  $241.5^\circ$ ;  $\text{C}_5\text{N}_2\text{H}_3\text{Cl}_3\text{O}$ , melting at  $282^\circ$ ;  $\text{C}_5\text{N}_2\text{H}_3\text{Cl}_3$ , melting at  $157.5^\circ$ ; and  $\text{C}_5\text{N}_2\text{H}_2\text{Cl}_4$ , melting at  $212^\circ$ . One of the chlorine-atoms of the last compound may be substituted by ethoxyl, and the compound  $\text{C}_5\text{N}_2\text{H}_2\text{Cl}_3\cdot\text{OEt}$  formed; it melts at  $83^\circ$ . By treating the tetrachloro-compound with hydrogen iodide, Ost's  $\gamma$ -hydroxypyridine is formed. A. P.

**Methylhydroxyglutaric Acid from Levulinic Acid and the corresponding Lactonic Acid.** By K. KRECKELER and B. TOLLENS (*Ber.*, **18**, 2018—2020).—By repeatedly digesting levulinic acid with rather more than the equivalent quantity of potassium cyanide, first at the ordinary temperature, and towards the end of the reaction at  $80$ — $100^\circ$ , and treating the resulting cyanide with hydrochloric acid, the authors have obtained an acid of the formula  $\text{C}_6\text{H}_{10}\text{O}_5$ , which readily loses water and is converted into the lactonic acid  $\text{C}_6\text{H}_8\text{O}_4$ . These acids proved to be identical with the methylhydroxyglutaric acid and its lactonic acid, obtained by Fittig and Bredt (*Abstr.*, 1882, 34) from isocapro lactone. The acid  $\text{C}_6\text{H}_8\text{O}_4$ , obtained by Kiliani from saccharone (*Abstr.*, 1883, 962), is not identical with the lactonic acid.

A. J. G.

**Action of Phosphoric Chloride on Meconic Acid.** By E. HILSEBEIN (*J. pr. Chem.* [2], **32**, 129—153).—The author investigated this reaction in hopes of obtaining a chlorochelidonic acid by the replacement of the hydroxyl-group by chlorine; this compound was, however, not formed.

When meconic acid (1 mol.) is heated with phosphoric chloride (5 mols.) and phosphoric oxychloride (the latter serving only as a solvent for the meconic acid), a liquid chloride,  $\text{C}_5\text{HCl}_6(\text{COCl})_2$ ? is formed; when this is treated with ice-water, it yields an acid of the formula  $\text{HO}\cdot\text{C}_5\text{ClO}(\text{COOH})_2$ , whilst with water at  $70^\circ$ , much oxalic acid and uncrystallisable products are formed.

*Chloromeconic acid*,  $\text{HO}\cdot\text{C}_5\text{ClO}(\text{COOH})_2 + \text{H}_2\text{O}$ , prepared as above, is obtained in prismatic crystals resembling those of gypsum; it melts at  $165^\circ$  with decomposition, is sparingly soluble in water, readily soluble in alcohol and ether. Its aqueous solution has a strongly acid reaction, and gives an intense dark-green coloration with ferric chloride. The yield is about 13 per cent. of the meconic acid employed. The *monethyl* salt,  $\text{COOH}\cdot\text{C}_5\text{ClO}(\text{OH})\cdot\text{COOEt}$ , crystallises in lustrous needles, melts at  $148^\circ$ , and can be sublimed. With ferric



chloride it gives a dirty-green coloration, changing to red on heating. When heated with acetic anhydride, it gives an *acetyl* compound,  $\text{COOH} \cdot \text{C}_5\text{ClO}(\text{OAc}) \cdot \text{COOEt}$ , crystallising in concentrically grouped, slender, lustrous needles, and melting at  $70^\circ$ . The *hydrogen barium* salt,  $(\text{C}_7\text{H}_2\text{ClO}_6)_2\text{Ba}$ , crystallising in long prisms, and a *basic barium* salt,  $(\text{C}_7\text{ClO}_6)_2\text{Ba}_3$ , forming a yellowish-white crystalline powder, were obtained.

*Chloropyromecenic acid*,  $\text{C}_5\text{H}_2\text{ClO} \cdot \text{OH} + \text{H}_2\text{O}$ , prepared by the dry distillation of chloromecenic acid, crystallises in long pale yellow prisms, melts at  $174^\circ$ , but sublimes even at the ordinary temperature; it is sparingly soluble in water, readily in alcohol and ether, and gives a dark green coloration with ferric chloride. The *calcium* salt,  $(\text{C}_5\text{H}_2\text{ClO} \cdot \text{O})_2\text{Ca}$ , crystallises in nodular groups of needles.

Whilst dilute ammonia converts chloromecenic acid into its ammonium salt, the action of excess of concentrated ammonia leads to the formation of a blue colouring matter, soluble in alkalis, and reprecipitated by acids, and of a red colouring matter which is obtained from the filtrate from the last by extraction with ether; neither could be crystallised.

*Chlorodihydrumecenic acid*,  $\text{HO} \cdot \text{C}_5\text{H}_2\text{ClO}(\text{COOH})_2$ , is obtained by the action of sodium amalgam on an acid solution of chloromecenic acid. It crystallises in tufts of prisms, melts at  $145^\circ$  with partial decomposition, is sparingly soluble in water, readily in alcohol and ether, and gives a clear green coloration with aqueous ferric chloride.

It was not found possible to replace the chlorine in chloromecenic acid by hydrogen without, at the same time, replacing the hydroxyl and adding 8 atoms of hydrogen. When heated with fuming hydroiodic acid at  $100^\circ$ , *hydroxyamylenedicarboxylic acid*,  $\text{C}_6\text{H}_9\text{OH}(\text{COOH})_2$ , is obtained. This crystallises in hard, transparent, colourless, spear-shaped forms, and sublimes at a higher temperature, melts at  $149^\circ$ , is sparingly soluble in cold, readily in hot water and in alcohol or ether, insoluble in chloroform and benzene. It has an acid reaction, and gives no coloration with ferric chloride. The silver salt,  $\text{C}_6\text{H}_9\text{O}(\text{COOAg})_2$ , is a white crystalline powder. The *ethyl* salt,  $\text{C}_6\text{H}_9\text{O}(\text{COOEt})_2$ , is a colourless thick liquid; it boils at  $250^\circ$ , and is insoluble in water, soluble in alcohol and ether. When heated with lime, hydroxyamylenedicarboxylic acid yielded a small quantity of a colourless liquid boiling at  $129$ – $130^\circ$ , and of an odour resembling that of fusel oil; on analysis, it gave numbers agreeing with those required for an amyl alcohol, but the amount obtained was too small to identify it. A. J. G.

**Nitrogenous Derivatives of Comenic Acid.** By E. MENNEL (*J. pr. Chem.* [2], 32, 176–186).—*Phenylcomenamic acid*,  $\text{C}_{12}\text{H}_9\text{NO}_4 + \text{H}_2\text{O}$ , is obtained by heating an aqueous solution of comenic acid with aniline. It crystallises in colourless tetrahedrons, is soluble in water, and gives a violet coloration with ferric chloride. *Ethylcomenamic acid*,  $\text{C}_8\text{H}_9\text{NO}_4 + 2\text{H}_2\text{O}$ , prepared in a similar manner from ethylamine and comenic acid, crystallises in large colourless prisms, melts at  $210^\circ$  with evolution of gas, and gives a violet coloration with ferric chloride. *Ethyl ethylcomenamate hydrochloride*,  $(\text{C}_8\text{H}_9\text{NO}_4\text{Et})_2\text{HCl}$ ,

is obtained by treating an alcoholic solution of the acid with hydrogen chloride; it crystallises in aggregates of colourless needles; when treated with aqueous soda, it yields the free acid, whilst with alcoholic soda it yields the *ethyl* salt,  $C_8H_9NO_4Et$ ; the latter crystallises in colourless needles, and melts at  $114-115^\circ$ . When ammonia and barium chloride are added to the hydrochloride, long, thin needles of the formula  $(C_{10}H_{12}NO_4)_2Ba + H_2O$  are obtained.

*Acetylethylpyromeconamic acid*,  $C_9H_{11}NO_3$ , is obtained by heating ethylcomenamic acid with acetic anhydride in sealed tubes at  $160^\circ$ . It crystallises from benzene in prismatic forms containing 1 mol. of benzene, which it loses at  $80^\circ$ ; it melts at  $140^\circ$ .

*Ethylpyromeconamic acid*,  $C_7H_9NO_2$ , is obtained by boiling the acetyl compound with water, or by heating ethyl comenamate at  $210^\circ$ ; it crystallises in needles, melts at  $166^\circ$ , is readily soluble in water, alcohol, and chloroform; less readily in benzene, and is not decomposed when heated with hydrochloric acid at  $240^\circ$ . When oxidised with potassium permanganate, it yields oxalic acid and ethylamine. A small quantity of ethylamine is also formed when it is treated with sodium amalgam.

A. J. G.

**Sulphopyromucic Acid.** By H. B. HILL and A. W. PALMER (*Ber.*, 18, 2095—2097).— $\delta$ -Sulphopyromucic acid is obtained by slowly adding pyromucic acid to fuming sulphuric acid. It crystallises in deliquescent prisms, and yields oxalic and succinic acids when fused with potash. The barium salt, contrary to the statement of Schwanert (*Annalen*, 116, 268), crystallises in globular aggregates of small prisms of the formula  $BaC_5H_2SO_6 + 4H_2O$ . The lead salt,  $PbC_5H_2SO_6 + 2H_2O$ , and the silver salt,  $Ag_2C_5H_2SO_6$ , are also described. When the barium salt is treated with bromine-water, it is converted into barium sulphate and fumaric acid.

An acid of the formula  $COOH \cdot C_4Br_2O \cdot SO_3H$  is obtained by the action of fuming sulphuric acid on  $\beta$ - $\gamma$ -dibromopyromucic acid (*Abstr.*, 1884, 1305). The barium salt,  $BaC_5Br_2SO_6 + 5H_2O$ , crystallises in long slender needles, and when treated in aqueous solution with bromine yields barium sulphate and dibrommaleic acid. When the dibrom-acid is treated with zinc in ammoniacal solution,  $\delta$ -sulphopyromucic acid is formed.

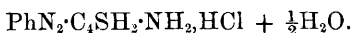
When  $\delta$ -monobromopyromucic acid is dissolved in fuming sulphuric acid, a sulphobromopyromucic acid is obtained crystallising in long deliquescent needles; its barium salt has the formula  $BaC_5HBrSO_6 + 5H_2O$ . When the acid is treated with zinc-dust in ammoniacal solution, it yields  $\beta$ -sulphopyromucic acid, isomeric with that described above. The barium salt,  $BaC_5H_2SO_6 + H_2O$ , crystallises in concentric groups of small prisms.

A. J. G.

**Compounds of Thiophen.** By O. STADLER (*Ber.*, 18, 2316—2320).—*Thiophenine (amidothiophen) hydrochloride*,  $C_4SH_3 \cdot NH_2 \cdot HCl$ , is prepared by suspending the stannochloride (this vol., p. 972) in the least possible quantity of water, decomposing with hydrogen sulphide and evaporating the filtrate in a vacuum over sulphuric acid and soda; it crystallises in long lustrous needles. When heated with

acetic chloride, it yields a dark-red powder which, if rubbed, shows the coppery lustre characteristic of the aniline dyes. It is soluble in concentrated sulphuric or acetic acids with magenta colour, but is insoluble in most other solvents; it could not be purified.

When a solution of thiophenine hydrochloride is mixed with aqueous diazobenzene chloride, a precipitate is obtained of a substance crystallising in yellow, microscopic needles of the formula



This is soluble in water and alcohol, and does not yield nitrogen when boiled with hydrochloric acid. A similar compound crystallising in microscopic, red needles is obtained by the action of  $\alpha$ -diazonaphthalene on the hydrochloride. It is not very soluble in water and alcohol, and dyes silk. A yellow dye is also obtained by the action of diazobenzenesulphonic acid; it crystallises in red needles.

*Nitrothienol*,  $\text{NO}_2\cdot\text{C}_4\text{SH}_2\cdot\text{OH}$ , is obtained by the action of potassium nitrite on the hydrochloride, the mixture being at first cooled with ice, but afterwards heated on the water-bath. It crystallises in colourless needles, melts at  $115-116^\circ$ , dissolves in alkalis with yellow colour, and closely resembles paranitrophenol in most of its properties. The yield is very small, much resin being formed.

A mixture of thiophenine hydrochloride and methyl alcohol when heated in sealed tubes at  $250-280^\circ$  gave, not as was hoped, dimethylthiophenamine, but methyl mercaptan and carbonaceous products.

A. J. G.

**Thioxylen from Coal Tar.** By J. MESSINGER (*Ber.*, 18, 2300—2303).—*Acetothioxylen*,  $\text{C}_4\text{SHMe}_2\text{Ac}$ , is prepared by treating 5 grams of thioxylen, diluted with 100 grams of light petroleum with 3.5 grams of acetic chloride, small quantities of aluminium chloride being added from time to time; the mixture is occasionally heated on the water-bath. It is a colourless liquid of sp. gr. 1.0910 at  $17^\circ$  (water at  $17^\circ = 1$ ) and has not a disagreeable odour; it boils at  $223-224^\circ$  (uncorr.), and soon becomes discoloured on exposure to air. It gives a red coloration with isatin and sulphuric acid.

*Dimethylthienylmethylacetoxime*,  $\text{C}_4\text{SHMe}_2\cdot\text{CMe}:\text{NOH}$ , is obtained by the action of hydroxylamine hydrochloride and sodium ethoxide on an alcoholic solution of acetothioxylen; it crystallises in thick white needles, and melts at  $65^\circ$ . Phenylhydrazine reacts with acetothioxylen, but the product could not be crystallised.

Acetothioxylen, when oxidised with potassium permanganate, yields a mixture of products from which, by solution in ammonia, boiling with animal charcoal, and precipitation with silver nitrate, a yellow silver salt was obtained, which, when treated with ether and methyl iodide, yielded *methyl thiophentricarboxylate*,  $\text{C}_4\text{SH}(\text{COOMe})_3$ . It crystallises in plates, melts at  $118^\circ$ , and is readily soluble in alcohol and ether. The free acid could not be prepared from want of material.

A. J. G.

**Synthesis of Thioxylen and Pyrroline-derivatives.** By C. PAAL (*Ber.*, 18, 2251—2254).—A thioxylen possibly identical with Messinger's (this vol., p. 1052) may be obtained by heating acetonyl-

acetone (this vol., p. 505) with finely powdered phosphorous pentasulphide in a reflux apparatus; it forms a colourless, mobile liquid having a slightly unpleasant odour, and boils at  $134-135^{\circ}$  (uncorr.). The pure compound readily dissolves sulphur; with isatin and sulphuric acid, it forms a cherry-red coloration, becoming reddish-brown when heated; on adding the compound and concentrated sulphuric acid to a solution of phenanthraquinone in glacial acetic acid, a magnificent violet coloration is formed, and by the addition of the thioxylene to a solution of benzoylformic acid in concentrated sulphuric acid, a dark reddish-brown coloration is formed.

*Dibromothioxylene*,  $C_4SBr_2Me_2$ , is obtained by adding the theoretical amount of bromine to a solution of thioxylene, both in solution in carbon bisulphide; it crystallises in large needles, softens at  $47^{\circ}$ , and melts at  $50^{\circ}$ .

*Tribromothioxylene* may be prepared by dissolving the dibromo-derivative in excess of bromine and allowing it to remain for 12 hours; it crystallises from alcohol in slender white needles, and melts at  $142-144^{\circ}$ .

By the oxidation of thioxylene with an alkaline solution of potassium permanganate, *methylothiophencarboxylic acid*,



is formed; it melts at  $142^{\circ}$ , is readily soluble in alcohol, ether, and boiling water, and crystallises from the latter in white needles, sublimes at  $120^{\circ}$ , and yields no colour reaction with isatin and sulphuric acid. The *silver salt* forms a white, crystalline powder, somewhat soluble in water. When acetonylacetone is heated with a slight excess of alcoholic ammonia in sealed tubes for an hour at  $150^{\circ}$ , dimethylpyrrolone, identical with that obtained by Weidel and Ciamician (Abstr., 1880, 404), and Knorr (this vol., p. 995), is formed.

A. P.

**Bromination of  $\alpha$ - and  $\beta$ -Thiophenic Acids.** By R. BONZ (Ber., 18, 2308—2315).—Dibrom- $\alpha$ -thiophenic acid is described by Peter (this vol., p. 765) as melting at  $209-211^{\circ}$ . The *dibromo- $\beta$ -thiophenic acid*, prepared from  $\beta$ -thiophenic acid, melts at  $220-222^{\circ}$ . The author finds that there appears to be complete identity in the crystalline form and all other properties, of these two acids, except melting point, and that their derivatives—of which a large number were prepared and compared—also show complete identity. The author prepared the  $\alpha$ -acid according to Peter's directions, and found the melting point, after repeated recrystallisation, to be  $212-213^{\circ}$ ; if, however, this  $\alpha$ -dibromo-acid is converted into the amide or into the methyl salt, and these compounds are then saponified, &c., the acid obtained shows the melting point  $220-221^{\circ}$ . The author therefore thinks that these acids must be identical. The following derivatives were prepared in each case from both the  $\alpha$ - and  $\beta$ -acids. *Barium salt*,  $(C_5SHBr_2O_2)_2Ba + 3\frac{1}{2}H_2O$ , crystallises in needles. The *silver salt*,  $C_5SHBr_2O_2Ag$ , a granulo-crystalline powder. The *methyl salt*,  $C_4SHBr_2 \cdot COOMe$ , crystallises in needles and melts at  $80-80.5^{\circ}$ . *Dibromothiophenic chloride* crystallises in silky needles, and melts at  $35.5-39.5^{\circ}$ . *Dibromothiophenamide*,  $C_4SHBr_2 \cdot CONH_2$ , crystallises in slender, white, interlaced needles, and melts at  $165.5-167^{\circ}$ .

**Remarks on the Preceding Paper.** By VICTOR MEYER (*Ber.*, 18, 2315—2316).—The unexpected results described above, led to a comparison of  $\alpha$ - and  $\beta$ -thiophenic acids, which showed that they certainly differ in melting point, and also in their solubilities in water; nevertheless all the derivatives of these acids—such as bromine-derivatives, ketones prepared by distillation, &c., show no marked differences. Whether the isomerism between the  $\alpha$ - and  $\beta$ -acids is physical, or whether the resemblance in properties of the derivatives is only accidental, or, lastly, whether the  $\alpha$ -acid, although apparently pure, may be contaminated with some very adherent impurity in quantity too small to be detected by analysis, can only be settled by further investigation. Gattermann is continuing the research with this object.

A. J. G.

**Action of Ethyl Chlorocarbonate and Sodium Amalgam on Di-iodothiophen.** By R. NAHNSEN (*Ber.*, 18, 2304).—It was thought that this reaction would lead to the formation of a thiophendicarboxylic acid, but only a considerable quantity of  $\beta$ -thiophenic acid was obtained together with traces of a solid acid.

A. J. G.

**Synthesis of Thiophendicarboxylic Acid.** By R. BONZ (*Ber.*, 18, 2305—2307).—As there is good reason to suppose that dibromothiophen is a para-compound, it was thought advisable, in the first place, to ascertain if paradibromobenzene would yield terephthalic acid when treated with ethyl chlorocarbonate and sodium amalgam—a reaction that has been shown to yield isophthalic acid in the case of metadibromobenzene together with metabromobenzoic acid (Wurster, this Journal, 1874, 369). Terephthalic acid is exclusively formed in the case of paradibromobenzene.

With dibromothiophen, the products of the action of ethyl chlorocarbonate and sodium amalgam are  $\beta$ -thiophenic acid, and a thiophendicarboxylic acid which proved to be identical with that obtained by Jaekel from thiophendisulphonic acid, and by Messinger from thioxylene (this vol., p. 767).

A. J. G.

**Action of Phosphoric Selenide on Acetylacetone.** By C. PAAL (*Ber.*, 18, 2255—2256).—*Selenoxylen*,  $C_4SeH_2Me_2$ , may be prepared by heating equal weights of acetylacetone and phosphorous pentaselenide in sealed tubes for an hour at  $180^\circ$ ; it is a heavy, colourless, mobile fluid, boils at  $153$ — $155^\circ$  (uncorr.), and has a slight disagreeable odour, somewhat similar to that of thioxylene; it dissolves in concentrated sulphuric acid with a reddish-brown colour, and, when dissolved in sulphuric acid containing isatin, exhibits a splendid dark carmine-red coloration; it also yields Laubenheimer's reaction, and is similar to thioxylene in its behaviour towards benzoylformic and sulphuric acids.

A. P.

**Action of Ethyl Diazoacetate on Aromatic Hydrocarbons.** By E. BUCHNER and T. CURTIUS (*Ber.*, 18, 2377—2379).—The authors formerly stated that the diazoacetates did not act on aromatic hydrocarbons; they now find that this statement is true only when the hydrocarbon is present in small quantity; if, however, the hydrocarbon

is present in large quantity, then the diazoacetate reacts with it: the more completely, the larger the excess of the hydrocarbon.

When a mixture of ethyl diazoacetate (40 grams) and toluene (160 grams) is heated in a reflux apparatus until nitrogen ceases to be evolved, and the product, after distilling off the toluene, is distilled with steam, a residue of ethyl azinsuccinate is left, whilst a strongly smelling oil goes over, which, after washing, distils nearly completely between 235° and 245°. This substance has the formula  $C_{11}H_{14}O_2$ , and boils at 238—239° under 725·5 mm. pressure; when saponified, it yields ethyl alcohol and an acid, a colourless, thick oil, which does not crystallise at -5°. This distils at 268—275° under 720 mm. pressure with scarcely any decomposition, and also distils readily with steam; it is sparingly soluble in hot water, readily soluble in alcohol and ether; its silver salt forms a white crystalline precipitate.

A substance of the formula  $C_{12}H_{16}O_2$  is prepared in similar manner from orthoxylene; it boils at 254—257° under 725 mm. pressure.

Benzene when heated with ethyl diazoacetate, yields a similar compound; the acid prepared from this is readily volatile, but cannot be crystallised. The constitutions of these substances are under investigation.

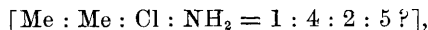
A. J. G.

**Action of Fuming Nitric Acid on Paraxylylene Bromide.** By W. Löw (*Ber.*, 18, 2072—2075).—In this reaction, unlike that with benzyl chloride, the fuming nitric acid exerts an oxidising action only, no nitro-derivatives being formed. The products of the reaction are terephthalic aldehyde, terephthalaldehydic acid, and a compound of the formula  $C_{12}H_{10}Br_2O_4$ , apparently an intermediate product. This substance crystallises in needles, melts at 80°, and is insoluble in water, readily soluble in ether, chloroform, and benzene. It yields a soluble compound with hydrogen sodium sulphite, and, when heated with water, is resolved into terephthalic aldehyde, hydrobromic acid, and tolylene alcohol. It therefore probably has the constitution  $C_6H_4(CH_2 \cdot O \cdot CHBr \cdot C_6H_4 \cdot COH)_2$ .

A. J. G.

**Mono- and Di-chloroxylylene. Chloroparaxylylidine.** By P. KLUGE (*Ber.*, 18, 2098—2099).—In the preparation of amido-compounds by the reduction of aromatic nitro-derivatives by tin and hydrochloric acid, monochloro-derivatives of the amines are known to be also formed, but their constitution has never been determined.

Nitroparaxylylene when heated on the water-bath with tin and concentrated hydrochloric acid, yields the chloroparaxylylidine,



described by Jannasch (*Annalen*, 176, 55). This, when boiled for several hours with glacial acetic acid, yields *acetochloroparaxylylide*,  $C_6H_2Me_2Cl_2 \cdot NH_4Ac$ , crystallising in colourless needles, and melting at 171°.

*Dichloroparaxylylene*,  $C_6H_2Me_2Cl_2$  [ $Me_2 : Cl_2 = 1 : 4 : 2 : 5 ?$ ], is prepared by converting chloroparaxylylidine into the diazo-compound and treating this with cuprous chloride and hydrochloric acid. It crystallises in plates or flat needles, melts at 71°, and boils at 221°; it is

sparingly soluble in cold, readily soluble in hot alcohol and in ether. When nitrated, it yields *dinitrodichloroparaxylylene*, crystallising in small needles, and melting at  $225^{\circ}$ .

Chloroparaxylylene, prepared by the direct chlorination of paraxylylene, boils at  $186^{\circ}$  under 767 mm. pressure, and solidifies in a freezing mixture to a crystalline mass melting at  $2^{\circ}$ . The sulphonic acid prepared from it crystallises well; its barium salt crystallises in needles; the sodium salt in prisms; both containing 1 mol.  $\text{H}_2\text{O}$ . On further chlorination the monochloro-derivative yields a dichloroparaxylylene identical with that described above. The chlorine-atoms are most probably in the 2 : 5 position, as it has been shown that the bromine-atoms occupy those positions in the dibromo-derivative formed by direct bromination.

A. J. G.

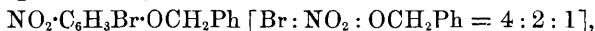
**Presence of Pseudocumene and Mesitylene in Different Mineral Oils.** By C. ENGLER (*Ber.*, **18**, 2234—2238).—That portion of Pennsylvanian oil boiling at  $170$ — $190^{\circ}$ , contains about 0.2 per cent. of these hydrocarbons; a smaller quantity was also found in the fractions  $150$ — $170^{\circ}$  and  $190$ — $210^{\circ}$ . Baku oil contains about 0.1 per cent.; small quantities were also found in the oils from Alsace, Galicia, and Italy.

N. H. M.

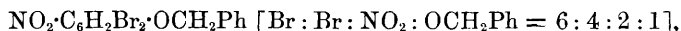
**Reactions dependent on Position.** By C. LIEBERMANN and ST. V. KOSTANECKI (*Ber.*, **18**, 2142—2149).—A theoretical paper, tracing the relation between the reactions and properties of some hydroxylated aromatic substances, and the positions of the hydroxyl groups.

A. J. G.

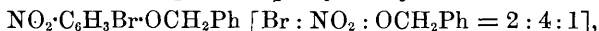
**Benzyl Ethers of Brominated Nitrophenols and their Behaviour on Reduction.** By G. ROLL and O. HÖLZ (*J. pr. Chem.* [2], **32**, 56—61).—The following benzyl ethers of the brominated nitrophenols were prepared by heating metallic derivatives of the corresponding nitrophenols with benzyl chloride in the presence of alcohol for 6—8 hours at  $100^{\circ}$ ; the reaction takes place more rapidly in sealed tubes at  $150^{\circ}$ , but the product is not so pure. *Monobrom-orthonitrophenyl benzyl ether*,



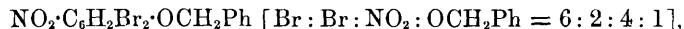
crystallises from alcohol in thick, clear yellow prisms, it melts at  $83.5^{\circ}$  (uncorr.), is insoluble in water, but readily soluble in alcohol. *Dibrom-orthonitrophenyl benzyl ether*,



crystallises in large, compact, yellow, monoclinic crystals, melts at  $64.5^{\circ}$  (uncorr.) and is insoluble in water, but dissolves readily in alcohol, ether, &c. *Monobromo-paranitrophenyl benzyl ether*,



crystallises in nearly colourless lustrous tablets, melts at  $125.5^{\circ}$  (uncorr.), is insoluble in water but soluble in ether, alcohol, &c. *Dibromo-paranitrophenyl benzyl ether*,



crystallises in colourless, long, brittle needles, melts at  $93.5^{\circ}$ , is insoluble in water, but dissolves readily in alcohol, ether, &c. All the above benzyl ethers are reduced by the action of tin and hydrochloric acid, being at the same time saponified, benzyl chloride and the amidophenols being formed; alcoholic ammonium sulphide has no action on the ethers; zinc-dust and soda form dark brown tarry reduction products, whilst sodium amalgam yields a small quantity of a white, crystalline substance; this melts at  $79-80^{\circ}$ , and may possibly consist of an amido-compound of the benzyl ethers. A. P.

**Carvoxime.** By H. GOLDSCHMIDT and R. ZÜRRER (*Ber.*, **18**, 2220—2223, comp. this vol., p. 1058).—Hesperidine nitrosyl chloride when boiled with alcohol yields carvoxime. It is quite insoluble in soda, whilst the isomeric hydrochlorocarvoxime dissolves in cold soda solution, from which it is precipitated by carbonic anhydride. Hydrochlorocarvoxime reacts with benzoic chloride with formation of *benzoyl-hydrochlorocarvoxime*,  $(\text{HCl})\text{C}_{10}\text{H}_{14}:\text{NOBz}$ . The latter compound crystallises from light petroleum in long, colourless, lustrous needles melting at  $114-115^{\circ}$ . On the other hand, hesperidine nitrosyl chloride does not react either with benzoic or with acetic chloride. This compound cannot therefore contain an oximide-group, and probably has the constitution  $(\text{HOH})\text{C}_{10}\text{H}_{14}:\text{NCl}$ .

Bromine acts on hesperidine nitrosyl chloride with formation of an *additive compound*,  $\text{C}_{10}\text{H}_{14}\text{NClBr}_2\text{O}$ , melting at  $130-131^{\circ}$ . Hydrochlorocarvoxime also yields an additive bromine-compound which is very unstable.

The behaviour of nitroso-terpene is in some respects analogous to that of its isomeric, carvoxime, and it probably contains the isonitroso-group; it does not, however, yield with hydrochloric acid a compound analogous to hydrochlorocarvoxime. N. H. M.

**Constitution of Chloranilic Acid.** By S. LEVY (*Ber.*, **18**, 2366—2371).—*Paradichloroparadibromoquinone*,  $\text{C}_6\text{Cl}_2\text{Br}_2\text{O}_2$  [ $\text{O}_2:\text{Cl}_2:\text{Br}_2 = 1:4:2:5:3:6$ ], is obtained by the action of bromine on a solution of paradichloroquinone in glacial acetic acid. It crystallises in reddish-brown, monosymmetric forms;  $a:b:c = 1.446:1:2.850$ ;  $\beta = 77^{\circ} 30'$ ; observed forms,  $0\text{P}$ ,  $\infty\text{P}\infty$ ,  $+2\text{P}\infty$ ,  $+ \text{P}$ , and is therefore not isomorphous with the meta-compound (*Abstr.*, 1883, 1117). It is insoluble in water, very sparingly soluble in ether and hot alcohol, soluble in benzene.

*Paradichloroparadibromoquinol*,  $\text{C}_6\text{Cl}_2\text{Br}_2(\text{OH})_2$ , is prepared from the quinone by heating it with stannous chloride; it crystallises in nearly colourless monosymmetric forms;  $a:b:c = 2.971:1:2.723$ ;  $\beta = 77^{\circ} 24'$ ; observed faces,  $0\text{P}$ ,  $\infty\text{P}\infty$ ,  $- \text{P}$ , and is therefore isomorphous with the meta-compound (*loc. cit.*). It melts at  $230^{\circ}$ . The *diacetyl*-derivative,  $\text{C}_6\text{Cl}_2\text{Br}_2(\text{OAc})_2$ , crystallises in slender, colourless needles, and melts at  $265^{\circ}$ . The *acetyl*-derivative of the meta-compound was also prepared; it closely resembles the foregoing and melts at  $269-270^{\circ}$ .

When paradichloroparadibromoquinone (5 parts) is moistened with alcohol and heated with a solution of 5 parts of potash in 150 parts of water, it is converted into a chlorobromanilic acid identical with



that obtained from metadichlorometadibromoquinone (*loc. cit.*). As this substance is derived from both the para- and meta-compounds, it must have the constitution  $[O:O:OH:OH:Cl:Br = 1:4:2:3:5:6]$ , whilst chloranilic acid must by analogy have the like constitution.

A. J. G.

**Bromamidophenols.** By O. HÖLZ (*J. pr. Chem.* [2], 32, 65—70). — *Orthobromo-paramidophenol*,  $NH_2 \cdot C_6H_3Br \cdot OH$  [ $Br:NH_2:OH = 2:4:1$ ], may be readily obtained by the reduction of the corresponding nitrophenol or its benzyl ether with tin and hydrochloric acid; it crystallises in short, white needles or thick prisms, which become brown on exposure to light; it is soluble in the usual solvents, and melts with partial decomposition at  $158^\circ$  (uncorr.). It is readily soluble in aqueous alkalis, forming crystalline compounds. The *hydrochloride*,  $OH \cdot C_6H_3Br \cdot NH_2 \cdot HCl$ , forms silver-grey scales. The *stannochloride*,  $(HO \cdot C_6H_3Br \cdot NH_2)_2 \cdot H_2SnCl_4$ , forms lustrous white scales. The *sulphate* forms small, brilliant prisms. By treating the free base with very dilute nitric acid, a deep blue solution is obtained, from which the *nitrate* slowly separates in lustrous scales. The *hydrobromide*,  $HO \cdot C_6H_3Br \cdot NH_2 \cdot HBr$ , crystallises readily in brilliant prisms. The *acetyl compound*,  $HO \cdot C_6H_3Br \cdot NHAc$ , is obtained by treating the base with excess of acetic anhydride; it crystallises from hot water in brilliant, thick needles and melts at  $157^\circ$  (uncorr.).

*Diorthobromo-paramidophenol*, prepared by reduction of the nitro-compound, has been described by Böhmer (Abstr., 1882, 398), and Mohlau (Abstr., 1884, 593). The *acetyl compound*,  $HO \cdot C_6H_2Br_2 \cdot NHAc$ , crystallises in lustrous scales, melts at  $173$ — $174^\circ$ , and is insoluble in cold water, but dissolves readily in alcohol.

6.4 *Dibromorthamidophenol*,  $HO \cdot C_6H_2Br_2 \cdot NH_2$  [ $Br:Br:NH_2:OH = 6:4:2:1$ ], is also obtained by the reduction of the corresponding nitrophenol or its benzyl ether; it forms long, thin, yellow needles, melts at  $91$ — $92^\circ$ , and is soluble in the usual solvents. The *hydrochloride* forms reddish-coloured scales or plates, and is readily soluble in water with partial decomposition. The *stannochloride*,  $(C_6H_2Br_2NO)_2 \cdot H_2SnCl_4$ , forms long colourless needles. The *hydrobromide* forms fine reddish needles. The *acetyl compound*,



crystallises in yellowish needles; it melts at  $186^\circ$ , and is soluble in the usual solvents.

A. P.

**Parabrom-orthamidophenol.** By F. SCHÜTT (*J. pr. Chem.* [2], 32, 61—64). — *Parabrom-orthamidophenol*,  $NH_2 \cdot C_6H_3Br \cdot OH$ , is obtained by reducing parabrom-orthonitrophenol with tin and hydrochloric acid; it forms pale yellow needles, is soluble in the usual solvents, and melts at  $128^\circ$ ; with ferric chloride its aqueous solution gives a deep cherry-red coloration, and after a time throws down a finely divided reddish-brown precipitate. The following salts of the base were prepared. The *hydrochloride*, *hydrobromide*, *nitrate*, and *sulphate*,  $(NH_2 \cdot C_6H_3Br \cdot OH)_2 \cdot H_2SO_4$ , are described. The *acetyl-derivative*,  $HO \cdot C_6H_3Br \cdot NHAc$ , prepared by treating the base with acetic anhydride, is obtained either as golden-yellow scales melting at  $177^\circ$

(uncorr.), or as white needles melting at  $179^{\circ}$ . When treated with potash or ammonia, the ammonium or potassium derivative,  $\text{NH}_4\cdot\text{O}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{NHAc}$  or  $\text{KO}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{NHAc}$ , are respectively obtained. The author, in opposition to the results obtained by Pfaff (Abstr., 1883, 802), finds that none of the bromine is removed when parabromonitrophenol is reduced with tin and hydrochloric acid. A. P.

**Metamido-phenetöl.** By P. WAGNER (*J. pr. Chem.* [2], **32**, 70—80).—*Metamido-phenetöl*,  $\text{EtO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  [ $\text{OEt} : \text{NH}_2 = 1 : 3$ ], may be obtained by the reduction of metanitro-phenetöl (Abstr., 1879, 237) with tin and hydrochloric acid. It forms a clear yellowish liquid, which distils at  $180\text{--}205^{\circ}$  under 100 mm. pressure; it becomes rapidly darkened on exposure to the air. The *stannochloride*,  $\text{C}_8\text{H}_{11}\text{NO}\cdot\text{HSnCl}_3$ , forms lustrous, transparent scales readily soluble in dilute acids. The *hydrochloride* forms silky, greyish needles; the *hydrobromide* grey, nodular masses. The *sulphate*,  $(\text{C}_8\text{H}_{11}\text{NO})_2\cdot\text{H}_2\text{SO}_4 + 1\frac{1}{2}\text{H}_2\text{O}$ , forms broad, yellowish needles. The *oxalate*,  $(\text{C}_8\text{H}_{11}\text{NO})_2\cdot\text{C}_2\text{H}_2\text{O}_4$ , was also prepared. The *acetyl compound*,  $\text{EtO}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , forms lustrous white scales having a faint tinge of red; it melts at  $96\cdot7^{\circ}$  (uncorr.), and is very sparingly soluble in water.

*Metadiazophenetöl* was obtained by treating a cold solution of metamido-phenetöl hydrochloride with sodium nitrite. It forms brown resinous clots.

*Meta-phenetölazo- $\beta$ -naphtholsulphonic acid*,



is formed on gradually adding a cold solution of sodium nitrite (1 mol.) to a well-cooled mixture of amidophenetöl hydrochloride (1 mol.) and  $\beta$ -naphtholsulphonic acid (1 mol.). After some time, the colouring matter is thrown down as a red precipitate on the addition of sodium chloride.

*Metadimethamidophenetöl*,  $\text{EtO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , was prepared by gradually adding aqueous potash to a solution of metamidophenetöl hydrochloride and methyl iodide in methyl alcohol at  $100^{\circ}$ . The free base is a clear yellow oil; it boils of  $247^{\circ}$  (uncorr.). A small quantity of a yellow, crystalline substance, probably  $\text{EtO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$ , is also formed. The *platinochloride* is a bright yellow flocculent precipitate.

*Nitrosometadimethamidophenetöl hydrochloride*,



may be prepared by gradually adding amyl nitrite to a well-cooled solution of metadimethamidophenetöl hydrochloride in alcohol and hydrochloric acid. It separates in golden-yellow scales, which on drying in air become more of a brownish hue; it is readily soluble in water and alcohol, but is insoluble in ether. A. P.

**Cyanhydrins of Nitroso-compounds.** By E. LIPPMANN and F. FLEISSNER (*Monatsh. Chem.*, **6**, 537—545).—The authors acted on a hot alcoholic solution of nitrosodimethylaniline with potassium

cyanide with the view of obtaining the corresponding azyline. Contrary to their expectations, the cyanhydrin of nitrosodimethylaniline,  $C_{17}H_{21}N_5O_2$ , was produced, ammonia and dimethylaniline being evolved. The crude cyanhydrin is collected on a funnel, washed with water, and recrystallised from alcohol, from which it is deposited in red crystals. The pure compound melts at  $221^\circ$ , and dissolves freely in chloroform. On reduction with nascent hydrogen, ammonium formate and dimethylphenylenediamine are produced. The cyanhydrin unites with benzene, nitrobenzene, toluene, aniline, quinoline, and phenol to form crystalline additive products, which are characterised by their metallic lustre; for instance,  $2C_{17}H_{21}N_5O_2 + C_6H_6$  crystallises in monoclinic plates. The benzene is expelled at  $130-140^\circ$ .

*Nitrosodiethylaniline cyanhydrin*,  $C_{21}H_{29}N_5O_2$ , forms small reddish-yellow crystals melting at  $170^\circ$ . When reduced with stannous chloride, it is converted into ammonium formate and diethylphenylenediamine. Only those nitroso-derivatives of tertiary bases in which the NO group is united directly to a C atom, combine with hydrocyanic acid, forming cyanhydrins. W. C. W.

**Action of Carbonyl Chloride on Ethenyldiphenyldiamine (Diphenylacediamine).** By M. LOEB (*Ber.*, 18, 2427—2428).—When the carbonyl chloride is in excess, a compound,  $C_{16}H_{12}N_2Cl_2O_2$ , is formed, whilst with excess of the diamine, a carbamide,



is obtained. The reaction is being further studied.

L. T. T.

**Triphenylamine.** By C. HEYDRICH (*Ber.*, 18, 2156—2158).—Triphenylamine is conveniently prepared by dissolving 3 grams of sodium in 40 grams of boiling diphenylamine; if a larger quantity of sodium be added, the whole is carbonised. 20 grams of bromine are then added, and the whole boiled for a quarter of an hour longer. The liquid is now poured off from the sodium bromide and distilled: 3.5 grams of triphenylamine were obtained with much unchanged diphenylamine.

Benzotrichloride and zinc chloride act on triphenylamine with formation of a green basic substance. The solution in strong sulphuric acid is violet; in other acids and in alcohol, green.

*Trinitrotriphenylamine*,  $N(C_6H_4NO_2)_3$ , is prepared by the action of fuming nitric acid on the triphenylamine. It crystallises from nitrobenzene on addition of alcohol in plates which melt at  $280^\circ$ .

*Triamidotriphenylamine*,  $N(C_6H_4NH_2)_3$ , forms colourless needles melting at  $230^\circ$ . The *hydrochloride* forms colourless needles which become slightly blue on exposure to air. With ferric chloride, it acquires a fine blue, and with chloranil a blue-green colour. The *acetyl-derivative*,  $N(C_6H_4NHAc)_3$ , crystallises in needles which do not melt at  $240^\circ$ . N. H. M.

**Action of Dilute Nitric Acid on Anilides.** By L. M. NORTON and W. ALLEN (*Ber.*, 18, 1995—1999).—Methylacetanilide when

heated with a large excess of dilute nitric acid (sp. gr. 1.029) yields a dinitromethylaniline,  $C_6H_3(NO_2)_2 \cdot NHMe$ , forming yellow crystals and melting at  $175^\circ$ , probably identical with that obtained by Leymann (Abstr., 1882, 1057), although when treated with bromine it yields not a bromodinitraniline, but a *bromodinitromethylaniline*,



melting at  $147^\circ$ . This has the constitution  $[NHMe : NO_2 : NO_2 : Br = 1 : 2 : 4 : 6]$ , as it yields the known bromodinitrophenol of m. p. 114— $115^\circ$  when boiled with dilute aqueous potash.

Ethylacetanilide when treated with dilute nitric acid (sp. gr. 1.029) yields the dinitroethylaniline prepared by Romburgh (*Ber.*, 16, 1496) by the action of ethylamine on  $\alpha$ -dinitrobromobenzene.

Phenylacetanilide (acetdiphenylamine) when boiled with dilute nitric acid yields *trinitrodiphenylamine*,  $C_{12}H_8N_4O_6$ . This crystallises in yellow needles, melts at  $135^\circ$ , is insoluble in water, sparingly soluble in carbon bisulphide, and readily soluble in alcohol, benzene, nitrobenzene, ethyl acetate, and acetic acid.

Methylpropionanilide when boiled with nitric acid yields dinitromethylaniline, identical with that obtained from methylacetanilide. The same product is obtained, although with difficulty, from methylbenzanilide.

Benzoyldiphenylamine (phenylbenzanilide) is only attacked with great difficulty by dilute nitric acid, the product of the reaction being trinitrodiphenylamine.

A. J. G.

### Phenoxydiphenylphosphine and some of its Derivatives.

By A. MICHAELIS and W. LA COSTE (*Ber.*, 18, 2109—2118).—*Phenoxydiphenylphosphine*,  $PPh_2 \cdot OPh$ , isomeric with triphenylphosphine oxide, is prepared by heating phenol and diphenylchlorophosphine in an atmosphere of hydrogen. It is a colourless viscid oil of sp. gr. 1.140 at  $24^\circ$  (water at  $4^\circ = 1$ ). It boils at  $265$ — $270^\circ$  under 62 mm. pressure, but cannot be distilled without partial decomposition under the ordinary pressure. The vapour-density as determined under diminished pressure was 10.02, calculated for  $C_{18}H_{15}PO = 9.68$ . It does not solidify in a freezing mixture. It oxidises readily on exposure to air or oxygen, with formation of phenylic diphenylphosphinate. When heated with water, it is decomposed into phenol and diphenylphosphinous acid,  $PPh_2 \cdot OH$ , the latter then suffering further decomposition into diphenylphosphinic acid and triphenylphosphine. The same changes occur still more readily in presence of alkalis. A *dibromide* seems to be formed on treating a solution of phenoxydiphenylphosphine in carbon tetrachloride with a dilute solution of bromine. It was obtained as a honey-yellow resin, but could not be prepared in a state fit for analysis.

*Phenylic diphenylphosphinate* (phenoxydiphenylphosphine oxide),  $PPh_2 \cdot O \cdot OPh$ , is obtained as a bye-product in the preparation of phenoxydiphenylphosphine, or by the oxidation of phenoxydiphenylphosphine, or by the action of water on the bromide, or of phenol on diphenylchloroxyphosphine,  $OPPh_2Cl$ . It crystallises in small, colourless needles or short prisms, melts at  $135$ — $136^\circ$ , and boils at about  $310^\circ$  under 62 mm. pressure with partial decomposition. It is

nearly insoluble in water, moderately soluble in hot alcohol, and sparingly soluble in ether.

*Phenoxydiphenylphosphine sulphide*,  $\text{PPh}_2\text{S}\cdot\text{OPh}$ , obtained by mixing solutions of its components in carbon bisulphide, crystallises in short, slender needles or in small prisms, melts at  $124^\circ$ , and is sparingly soluble in cold, more readily in hot alcohol and in ether, readily in carbon bisulphide.

*Phenoxydiphenylphosphine selenide*,  $\text{PPh}_2\text{Se}\cdot\text{OPh}$ , prepared in manner similar to the above, crystallises in nearly colourless needles, melts at  $114\text{--}115^\circ$ , and is sparingly soluble in cold alcohol.

*Phenoxydiphenylbenzylphosphonium chloride*,  $\text{PPh}_2(\text{C}_7\text{H}_7)\text{Cl}\cdot\text{OPh}$ , is obtained, by heating a mixture of its components, as a yellowish crystalline powder, which softens at  $194^\circ$ , and melts at  $232\text{--}236^\circ$  with partial decomposition. When boiled with water, it yields phenol, hydrochloric acid, and *diphenylbenzylphosphine oxide*,  $\text{OPPh}_2\cdot\text{C}_7\text{H}_7$ , which crystallises in tufts of white needles and melts at  $192\text{--}193^\circ$ .

*Phenoxydiphenylmethylphosphonium iodide*,  $\text{PMePh}_2\text{I}\cdot\text{OPh}$ , is formed by heating phenoxydiphenylphosphine with an excess of methyl iodide in a reflux apparatus. It is a granulo-crystalline mass, melting at  $134\text{--}136^\circ$ , and yielding diphenylmethylphosphine oxide when boiled with water. Under some, as yet unknown, conditions the reaction with methyl iodide takes another course, leading to the formation of dimethyldiphenylphosphonium iodide.

*Diphenylbenzylphosphine dichloride*,  $\text{PPh}_2\text{Cl}_2\cdot\text{C}_7\text{H}_7$ , is obtained by the action of benzyl chloride on diphenylchlorophosphine as a brownish, crystalline powder, which yields diphenylbenzylphosphine oxide when boiled with water.

A. J. G.

**Tribenzylamine.** By R. LEUCKART (*Ber.*, 18, 2341—2344).—When benzaldehyde is heated with ammonium formate, tribenzylamine is formed, together with a nitrogenous, crystalline, indifferent substance, very sparingly soluble in the ordinary solvents, and a crystalline substance melting at  $52^\circ$  and still under investigation.

A. J. G.

**New Cumidine.** By W. ENGEL (*Ber.*, 18, 2229—2233).—Crude cumidine yields an *acetyl*-derivative which melts at  $112^\circ$ , from which a new *cumidine*,  $\text{C}_9\text{H}_{13}\text{N}$ , boiling at  $223\text{--}224^\circ$ , was obtained. The *hydrochloride*, *platinochloride*, and *nitrate* are described.

*Cumenol*,  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{OH}$ , is prepared by adding potassium nitrite to a cooled, very dilute solution of cumidine in sulphuric acid, and then heating. It boils at  $216\text{--}218^\circ$ , and gives no colour reaction with ferric chloride.

*Mononitracetcumidide*,  $\text{NO}_2\cdot\text{C}_6\text{HMe}_3\cdot\text{NHAc}$ , is prepared by nitration of the acetyl-derivative above described. It crystallises in dull yellow needles melting at  $131^\circ$ , and is very sparingly soluble in hot water, very readily in alcohol, less readily in ether.

*Dinitracetcumidide*,  $\text{C}_6\text{Me}_3(\text{NO}_2)_2\cdot\text{NHAc}$ , is prepared by the action of a large excess of fuming nitric acid on acetcumidide. It forms almost colourless needles, melts at  $204^\circ$ , and is insoluble in water, soluble in ether and in alcohol. Concentrated hydrochloric acid acts

on it with formation of a compound crystallising in gold-coloured, slender needles melting at  $78^{\circ}$ . It is probably *dinitrocumidine*.

*Monocumylcarbamide*,  $C_6H_5Me_3NH \cdot CO \cdot NH_2$ , is prepared by treating cumidine hydrochloride with potassium cyanate; it crystallises in white needles insoluble in water, soluble in ether and alcohol, and decomposes at about  $227^{\circ}$  without melting, with evolution of ammonia and formation of *dicumylcarbamide*,  $CO(NH \cdot C_6H_5Me_3)_2$ . This compound forms white, silky needles which melt above  $290^{\circ}$ .

*Dicumylthiocarbamide*,  $CS(NH \cdot C_6H_5Me_3)_2$ , is prepared by treating cumidine with an excess of carbon bisulphide. It is insoluble in water, sparingly soluble in ether, but dissolves more readily in alcohol. It melts at  $196^{\circ}$ . Boiling water decomposes it; concentrated hydrochloric acid converts it into a cumyl isothiocyanate.

N. H. M.

**Hydrazine Compounds.** By H. LIMPRICHT (*Ber.*, **18**, 2193—2196).—*Parahydrazinetoluenemetasulphonic acid*,  $N_2H_3 \cdot C_6H_3Me \cdot SO_3H$  [ $Me : N_2H_3 : SO_3H = 1 : 4 : 3$ ], is prepared by adding the diazo-compound to stannous chloride; it forms flesh-coloured, fine prisms. The *potassium* and *barium* salts form readily soluble plates and nodules.

*Parahydrazinetoluenedisulphonic acid*,  $C_6H_2Me(SO_3H)_2 \cdot N_2H_3$ , crystallises in nodules. The *hydrogen barium salt* (with  $2\frac{1}{2}$  mols.  $H_2O$ ) and the *normal barium salt* are described.

*Orthohydrazinetolueneparasulphonic acid*,  $N_2H_3 \cdot C_6H_3Me \cdot SO_3H$  [ $Me : N_2H_3 : SO_3H = 1 : 2 : 4$ ], forms groups of long needles, which become yellowish on exposure to air; it is readily soluble in hot water. The *potassium* and *barium* salts are described.

*Nitrotolylhydrazinesulphonic acid*,  $NO_2 \cdot C_6H_2Me(N_2H_3) \cdot SO_3H$  [ $Me : NO_2 : N_2H_3 : SO_3H = 1 : 2 : 4 : 5$ ], crystallises from water in pale-yellow plates. The *barium salt* (with 4 mols.  $H_2O$ ) is described.

*Nitrobenzenehydrazinesulphonic acid*,  $N_2H_3 \cdot C_6H_3(NO_2) \cdot SO_3H + H_2O$ , forms lustrous, brownish needles, sparingly soluble in hot water. Several salts were prepared. When reduced, *amidobenzenehydrazinesulphonic acid*,  $N_2H_3 \cdot C_6H_3(NH_2) \cdot SO_3H$ , is formed. The *hydrochloride*, *sulphate*, and *nitrate* of this compound are described.

By the action of nitrous acid on hydrazobenzenedisulphonic acid, large, yellowish needles of a diazo-compound,  $C_{12}H_{10}N_4S_2O_8 + H_2O$ , are formed. This substance has been already prepared by Balentine (*Abstr.*, 1880, 809), who assigned to it a formula with 2 mols.  $H_2O$ . It yields, when reduced, a *hydrazine* compound,  $OH \cdot C_6H_3(N_2H_3) \cdot SO_3H$ , in the form of small, yellow prisms sparingly soluble in water.

*Phenylhydrazinesulphonic acid*,  $N_2H_3 \cdot C_6H_4 \cdot SO_3H$ , is prepared by acting on phenylhydrazine with chlorosulphonic acid at  $160^{\circ}$ . It forms pale-yellow, lustrous plates. A *barium salt* is described.

N. H. M.

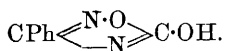
**Reactions of Amidoximes.** By F. TIEMANN (*Ber.*, **18**, 2456—2458).—A summary of the results described in the next five Abstracts.

**Action of Ethyl Chlorocarbonate and of Carbonyl Chloride on Benzenylamidoxime.** By E. FALCK (*Ber.*, **18**, 2467—2471).—

When a chloroform solution of benzenylamidoxime is acted on by carbonyl chloride, *ethyl benzenylamidoximecarbonate*,



is formed, together with benzenylamidoxime hydrochloride. The former is easily soluble in alcohol, benzene, ether, and chloroform; crystallises in needles, and melts at  $127^\circ$ . That the above is the correct formula is proved by the fact that the ethyl ether of benzenylamidoxime is not acted on by ethyl chlorocarbonate. The above salt is very unstable, and when heated, either alone or with water or dilute alkali, it yields alcohol and *benzenylazoxime carbinol*,



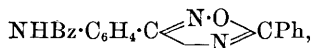
This crystallises in long needles which melt at  $197^\circ$ , and are easily soluble in alcohol, ether, and boiling water. The aqueous solution has an acid reaction. It does not form salts with acids, but dissolves in alkalis, and on heating even decomposes alkaline carbonates. *Silver, copper, and lead derivatives* were obtained.

When benzenylamidoxime is acted on by carbonyl chloride, *carbonyldibenzenylamidoxime*,  $\text{CO}(\text{O}\cdot\text{N}:\text{CPh}\cdot\text{NH}_2)_2$ , is formed. It crystallises in white scales easily soluble in alcohol and ether, sparingly in benzene, and insoluble in water; it melts at  $128\text{--}129^\circ$ . When heated with an alkali, it is converted into benzenylazoxime carbinol.

L. T. T.

**Derivatives of Metanitrobenzenylamidoxime and of Metanitrobenzylazoximebenzenyl.** By M. SCHÖPFF (*Ber.*, **18**, 2472—2477).—This is a continuation of the author's previous work (this vol., p. 896). *Metamidobenzenylamidoxime*, obtained by reducing the nitro-compound with stannous chloride, is a yellow crystalline substance, but was not obtained in a state pure enough for analysis. Its *hydrochloride* crystallises in prisms. Fehling's solution gives the dirty green copper precipitate characteristic of amidoximes. *Metamidobenzenylazoximebenzenyl*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{array}{c} \text{N}\cdot\text{O} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{CPh}$ , obtained by

the reduction of the nitro-compound by means of alcoholic ammonium sulphide, crystallises in long needles soluble in alcohol, ether, and benzene, insoluble in water; these melt at  $143^\circ$ , and sublime unchanged. Its *hydrochloride* is sparingly soluble in boiling water, and gives double chlorides with platinum, tin, and gold. When treated with benzoic chloride, it yields a *benzoyl-derivative*,



which is soluble in boiling alcohol, ether, and benzene, insoluble in water; it crystallises in needles, and melts at  $213^\circ$ . *Metahydroxybenzenylazoximebenzenyl*,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{array}{c} \text{N}\cdot\text{O} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{CPh}$ , was obtained from the amido-compound by means of the diazo-reaction. It forms pale-yellow needles melting at  $163^\circ$ , and sublimes unchanged. It is soluble in alcohol, benzene, ether, and chloroform, insoluble in water

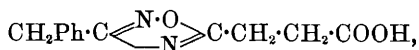
and light petroleum. Its *ethyl ether*,  $\text{EtO} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{CPh}$ , forms a woolly crystalline mass, which melts at  $71^\circ$ , and is insoluble in alkalis.

From the results of Falck's researches (see previous Abstract), the author ascribes the constitution  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NH}_2) : \text{N} \cdot \text{O} \cdot \text{COOEt}$  to the ethyl carbamate derivative described in his last communication (this vol., p. 898).

L. T. T.

**Derivatives of Phenylethenylamidoxime.** By P. KNUDSEN (*Ber.*, 18, 2482—2484).—This is a continuation of the author's previous work (this vol., p. 897). The ether of this amidoxime acts on carbanil to form *phenylethenylphenyluramidoxime ethyl ether*,  $\text{CH}_2\text{Ph} \cdot \text{C}(\text{NH} \cdot \text{CO} \cdot \text{NHPh}) : \text{N} \cdot \text{OEt}$ . This substance is soluble in alcohol, ether, benzene, and light petroleum, insoluble in water. It crystallises in small needles melting at  $148^\circ$ . It has acid, but not any basic properties. No satisfactory results have been obtained by the action of phenyl thiocyanate or of ethyl chlorocarbonate on the amidoxime. No action takes place at ordinary temperatures, but on heating, the action in each case becomes so violent that decomposition sets in.

*Phenylethenylazoximepropenylcarboxylic acid*,



is formed by the action of succinic anhydride on the parent amidoxime. It is a strong acid, dissolves readily in alcohol, ether, and boiling water, crystallises in scales or prisms, and melts at  $59$ — $60^\circ$ . *Silver* and *copper salts* are described.

L. T. T.

**Derivatives of Phenylhydroxyethenylamidoxime.** By F. GROSS (*Ber.*, 18, 2477—2482).—When a mixture of concentrated aqueous solutions of the hydrochloride of the above amidoxime and potassium cyanate is allowed to stand, *phenylhydroxyethenyluramidoxime*,  $\text{HO} \cdot \text{CHPh} \cdot \text{C}(\text{NOH}) \cdot \text{NH} \cdot \text{CONH}_2$ , crystallises out. It forms white scales or needles, soluble in water and alcohol, and melting at  $127^\circ$ . It dissolves both in acids and alkalis. *Phenylhydroxyethenylphenyluramidoxime*,  $\text{HO} \cdot \text{CHPh} \cdot \text{C}(\text{NOH}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$ , is obtained by the action of carbanil on the parent amidoxime. It forms minute, white needles melting at  $155^\circ$ , and is soluble in alcohol and ether, insoluble in water. Its basic and acid characters are very slight. Its *ethyl ether*,  $\text{HO} \cdot \text{CHPh} \cdot \text{C}(\text{NOEt}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$ , is formed when the free amidoxime in the above reaction is replaced by its ethyl ether. This crystallises in opaque white needles melting at  $119^\circ$ , and is soluble in alcohol, ether, and benzene, insoluble in water. It is insoluble in alkalis, and very sparingly soluble in hydrochloric acid. *Ethyl phenylhydroxyethenylamidoxime carbonate*,  $\text{OH} \cdot \text{CHPh} \cdot \text{C}(\text{NH}_2) : \text{N} \cdot \text{O} \cdot \text{COOEt}$ , is obtained by the action of the parent amidoxime on ethyl chlorocarbonate. It crystallises in minute, white needles which dissolve easily in alcohol, ether, and boiling water, and melt at  $106$ — $107^\circ$ . It dissolves in acid, but has no longer acid properties. The author



was unable to obtain from this compound a substance analogous to Falck's benzenylazoxime carbinol (this vol., p. 1217). A *carbonyl-derivative* of phenylhydroxyethenylamidoxime,

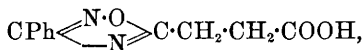


is obtained by the action of carbonyl chloride on the parent amidoxime. It yields glistening scales soluble in alcohol, very sparingly so in water and benzene, and melts at 131°. It dissolves in hydrochloric acid, but not in alkalis.

Phenyl thiocyanate does not act on phenylhydroxyethenylamidoxime at ordinary temperatures; but on heating a violent action sets in, and both substances are decomposed. Cyanogen converts the amidoxime into a black mass. Chlorocyanogen yields traces of a crystalline compound melting at 120°. L. T. T.

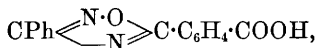
**Action of Anhydrides of Bibasic Acids on Benzenylamidoxime.** By O. SCHULZ (*Ber.*, **18**, 2458—2467).—In continuation of his previous work (this vol., p. 897), the author has studied the action of bibasic acids and their anhydrides on benzenylamidoxime. The free acids, like the monobasic acids, convert it into dibenzenylazoxime.

When succinic anhydride and benzenylamidoxime are heated together, *benzenylazoximepropenylcarboxylic acid*,



is formed. This acid is soluble in alcohol, chloroform, ether, and boiling water, crystallises in rhombic prisms or scales, and melts at 120°. It is very stable towards, and easily soluble in strong sulphuric acid. It forms well characterised salts. Its *chloride* could not be obtained in a pure state, as it decomposes at 128°, but the impure substance yielded the amide with ammonia. Amongst the decomposition-products obtained in attempts to distil the chloride, the author isolated kyaphenin. The *ethyl ether* is a pale-yellow aromatic oil boiling with partial decomposition at 255°. Crystals of kyaphenin separate out from the last portions of the distillate. The *amide* crystallises in needles melting at 168°. A small quantity of a substance melting at 160° was obtained as a bye-product in the above reaction.

*Benzenylazoximebenzenyl-ortho-carboxylic acid*,

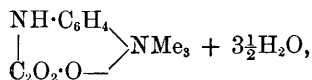


obtained by substituting phthalic anhydride for succinic anhydride in the previous reaction, crystallises in silky needles, soluble in ether, alcohol, and chloroform; it melts at 151°. A similar bye-product to that just described was obtained, and found to be dibenzenylazoxime. The proportion of the latter is very much increased if 2 mols. benzenylamidoxime are used to every one of phthalic anhydride. Various salts of the acid are described. The *chloride* is a heavy yellow oil which, on distillation, decomposes into kyaphenin, benzonitrile, and ammonium chloride. The *ethyl ether* is a heavy yellow oil

which cannot be distilled. The *amide* forms microscopic needles melting at 160°. L. T. T.

**Acidammonium Bases.** By P. GRIESS (*Ber.*, 18, 2408—2410).—The author gives this name to a new group of compounds obtained by replacing by methyl three atoms of hydrogen in Klusemann's metaphenylenoxamic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_2\text{O}_2\cdot\text{OH}$  (this Journal, 1875, 269), and analogous acids.

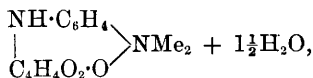
*Meta-oxalamidotrimethylphenylammonium,*



is obtained by half dissolving 1 part metaphenylenoxamic acid in methyl alcohol by means of aqueous potash, adding 2 parts methyl iodide, and allowing the mixture to stand for a week, care being taken to keep it alkaline. The product is then acidified with hydriodic acid and evaporated to a small bulk. On cooling, the *hydriodide* of the above bases crystallises in long, white needles with 1 mol.  $\text{H}_2\text{O}$ . It is easily soluble in boiling water, and yields a platinochloride crystallising in small needles or prisms. The free base, obtained by treating the hydriodide with silver carbonate, forms irregular hexagonal, micaceous plates or rhombic prisms. It is soluble in water and alcohol, insoluble in ether, and has a strong bitter taste. It loses its water of crystallisation at 115°, and at a slightly higher temperature is converted, with evolution of gas, into a volatile base which is soluble in alcohol, and crystallises in tetragonal tables. When treated with a solution of iodine in hydriodic acid, the original base yields a periodide crystallising in dark-brown microscopic needles.

*Para-oxalamidotrimethylphenylammonium*, obtained from paraphenylenoxamic acid (the latter was prepared by heating oxalic acid with aqueous paraphenylenediamine hydrochloride), crystallises with  $2\frac{1}{2}$  mols.  $\text{H}_2\text{O}$  in white, glistening needles or long, narrow scales, easily soluble in boiling water, sparingly in boiling alcohol, and insoluble in ether. It yields crystallisable salts.

*Meta-succinamidotrimethylphenylammonium,*



crystallises in white, hexagonal plates or prisms, easily soluble in cold water. It resembles the two bases just described. The *metaphenylenesuccinamic acid*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_4\text{H}_4\text{O}_2\cdot\text{OH}$ , from which it was obtained, was prepared by heating succinic acid with metaphenylenediamine hydrochloride. L. T. T.

**Phenylparamide.** By B. HÖTTE (*J. pr. Chem.* [2], 32, 238—239).—*Phenylparamide*,  $\text{C}_6(\text{C}_2\text{O}_2\cdot\text{NPh})_3$ , is obtained by heating mellitic acid with aniline for six to seven hours at 160°, or by heating aniline and ammonium mellitate for two days at 170°. It forms a white amorphous mass, does not melt at 300°, and is insoluble in the ordi-

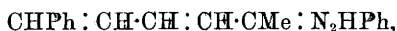
nary solvents; strong sulphuric acid dissolves it to a brown liquid, which decomposes on boiling.

By the action of methylamine on mellitic acid, only hydrogen methylammonium mellitate seems to be formed.

Phenylhydrazine reacts with phthalic anhydride, forming a compound crystallising in yellow needles, and melting at  $175-176^{\circ}$ ; it is being further investigated. A. J. G.

### Condensation-products of Cinnamaldehyde with Acetone.

By L. DIEHL and A. EINHORN (*Ber.*, **18**, 2320—2326).—*Cinnamenylvinyl methyl ketone*,  $\text{CHPh}:\text{CH}:\text{CH}:\text{CH}\cdot\text{COMe}$ , is best prepared by shaking a mixture of acetone (30 parts) dissolved in water (3600 parts) and cinnamaldehyde (40 parts), until a white emulsion is formed; 40 parts of 10 per cent. aqueous soda is then added, and the whole allowed to remain for 48 hours with occasional agitation, when the ketone crystallises out. When purified, it crystallises in large, rhombic plates, melts at  $68^{\circ}$ , is sparingly soluble in water, readily in the other ordinary solvents. It cannot be distilled, even under reduced pressure, and on exposure to air is converted into an oil of penetrating odour. The *phenylhydrazine-derivative*,

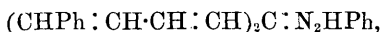


crystallises in citron-yellow plates of silky lustre, melts at  $180^{\circ}$ , and is sparingly soluble in ether and cold alcohol, readily soluble in hot alcohol, acetic acid, and ethyl acetate. The *dibromide*,



crystallises in microscopic needles, and melts at  $173.5^{\circ}$  with decomposition. When the ketone is heated at  $80-90^{\circ}$  with aqueous sodium hypochlorite and hydroxide, the mixture being constantly agitated, chloroform and Perkin's cinnamenylacrylic acid (this Journal, 1877, i, 403) are formed.

*Dicinnamenylvinyl ketone*,  $\text{CO}(\text{CH}:\text{CH}:\text{CH}:\text{CHPh})_2$ , is formed in the preparation of cinnamenylvinyl methyl ketone, but is more conveniently obtained by the condensation of the latter substance with cinnamaldehyde. It crystallises in golden-yellow needles, melts at  $142^{\circ}$ , is sparingly soluble in ether and cold alcohol, more readily in hot alcohol and in acetic acid and ethyl acetate; it dissolves in concentrated sulphuric acid with a splendid violet coloration, which disappears on dilution. The phenylhydrazine-compound,



crystallises in slender, interlaced, golden-yellow needles, and melts at  $166^{\circ}$ . A. J. G.

**Preparation of Ortho- and Para-nitrocinnamaldehyde.** By L. DIEHL and A. EINHORN (*Ber.*, **18**, 2335—2338).—A better yield of these substances is obtained by the direct nitration of commercial cinnamaldehyde than by methods starting from the corresponding nitrobenzaldehydes.

25 grams of cinnamaldehyde is stirred into a mixture of 500 grams  
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of sulphuric acid, with 20 grams of potassium nitrate, care being taken that the temperature does not rise too high. The liquid is then poured into water, when a mixture of the ortho- and para-nitraldehydes separates. The mixture is dissolved in boiling absolute alcohol, an equal volume of a solution of hydrogen sodium sulphite added, and the mixture allowed to cool. The greater part of the paranitrocinnamaldehyde compound then separates, and the remainder can be precipitated by adding a large amount of common salt, and allowing the whole to remain for 12 hours. The precipitate contains the excess of salt and the paranitro-compound, whilst the orthonitro-compound remains in solution. To separate the aldehydes from their hydrogen sodium sulphite compounds, these are dissolved in much water, and concentrated sulphuric acid added, when the aldehydes separate in flocks.

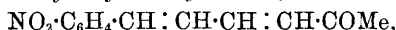
Paranitrocinnamaldehyde melts at 141—142°, and yields a phenylhydrazine-compound, which forms orange-red crystals and melts at 180—181°. When the aldehyde is reduced with ferrous sulphate and ammonia, and the product extracted with ether, an intense yellow liquid is obtained, which, when evaporated, yields a brownish-red substance of metallic lustre, probably a condensation-product.

The phenylhydrazine-derivative of orthonitrocinnamaldehyde crystallises in claret-coloured needles, and melts at 157·5°.

A. J. G.

**Condensation-products of Orthonitrocinnamaldehyde with Acetone.** By L. DIEHL and A. EINHORN (*Ber.*, **18**, 2326—2334).—Experiments made to nitrate the products described on the preceding page were unsuccessful, nothing but resinous products being obtained. The nitro-derivatives were therefore prepared by condensation from the nitraldehyde in a manner somewhat similar to that previously described.

*Orthonitrocinnamenylvinyl methyl ketone,*



crystallises in broad, pale-yellow needles, melts at 73·5°, and is readily soluble in most solvents. A well characterised reduction product could not be obtained.

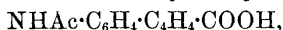
*Diorthonitrodicinnamenylvinyl ketone*,  $\text{CO}(\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , is obtained at the same time as the last-mentioned compound, from which it is separated by means of its sparing solubility in alcohol. It crystallises in very small, yellow needles, melts at 208·5°, and is readily soluble in acetone, chloroform, and hot acetic acid, less so in benzene, and scarcely soluble in alcohol, ether, and ethyl acetate.

A *ketone* of the formula  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CHPh}$  is obtained by condensation from cinnamenylvinyl methyl ketone and orthonitrocinnamaldehyde, in golden-yellow crystals, melting at 136·5°, and dissolving readily in acetone, chloroform, benzene, and acetic acid, sparingly in alcohol and ether.

*Orthonitrocinnamenylacrylic acid*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_2\text{H}_2\cdot\text{C}_2\text{H}_2\cdot\text{COOH}$ , is obtained by the action of an alkaline solution of sodium hypochlorite on orthonitrocinnamenylvinyl methyl ketone at 80—90°. It can also be directly prepared from orthonitrocinnamaldehyde by Perkin's reaction,

but the yield is not satisfactory. It crystallises in slender, interlaced needles, melts at  $217.5^{\circ}$ , and is insoluble in water, sparingly soluble in ether, readily soluble in acetic acid and hot alcohol. Its salts are of an intense yellow colour.

*Orthamidocinnamerylacrylic acid*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_4\text{H}_4 \cdot \text{COOH}$ , is obtained by reducing the nitro-acid with ferrous hydroxide in ammoniacal solution. It crystallises in yellow needles, melts at  $176.5^{\circ}$ , and is nearly insoluble in cold water, sparingly soluble in carbon bisulphide, readily soluble in alcohol, ether, chloroform, and glacial acetic acid. The ethereal solution has a strong green fluorescence. It yields salts with both acids and bases. The acetyl-compound,



crystallises in groups of small tables, and melts at  $253^{\circ}$  with decomposition. When the amido-acid is heated with acetic acid, saturated at  $0^{\circ}$  with hydriodic acid, quinoline seems to be formed.

A. J. G.

**Direct Formation of Orthonitracetophenone by the Nitration of Acetophenone.** By C. ENGLER (*Ber.*, **18**, 2238—2240).—When small quantities of acetophenone are nitrated at a temperature of  $30$ — $40^{\circ}$ , a product is obtained which yields metanitracetophenone and an oil consisting of orthonitracetophenone. The best conditions for obtaining the latter have not yet been ascertained, and the oil is sometimes contaminated with what is probably dinitracetophenone.

N. H. M.

**Derivatives of Dibromacetophenone.** By C. ENGLER and E. HASSENKAMP (*Ber.*, **18**, 2240—2245).—Dibromacetophenone is most conveniently prepared by gradually adding bromine in theoretical amount to a solution of acetophenone in glacial acetic acid, warming the mixture to  $65$ — $70^{\circ}$ , and pouring it into cold water.

*Dibromometanitracetophenone*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CHBr}_2$ , prepared by the action of nitric acid (1.4 sp. gr.) on the preceding compound, forms yellow tabular crystals, melts at  $59^{\circ}$ , and is soluble in the usual solvents.

On shaking a solution of dibromacetophenone in benzene with strong aqueous ammonia, benzamide and dibromethane are formed together with *isoidindileucine*,  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_{16}$ , a yellow crystalline substance isomeric with indileucine prepared from indirubin (*Abstr.*, 1884, 1028); it is very sparingly soluble in most of the usual solvents, and has basic properties, forming salts with concentrated acids which are decomposed by water. On the addition of phenol to its solution in concentrated sulphuric acid, a magnificent carmine-red coloration is produced. The picrate,  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH} + \text{H}_2\text{O}$ , crystallises in yellow needles, and melts at  $110$ — $115^{\circ}$ .

*Methylisoidindileucine*,  $\text{C}_{16}\text{H}_{11}\text{MeN}_2\text{O}$ , is obtained by heating isoidindileucine with excess of methyl iodide and alcoholic potash in sealed tubes at  $100$ — $110^{\circ}$ ; it crystallises in colourless scales and melts at  $115^{\circ}$ , and is soluble in ether and alcohol, but insoluble in water.

*Hydroisoidindileucine*,  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}$ , is obtained in the form of white crystalline scales by reducing isoidindileucine with tin and hydrochloric acid; it melts at  $160^{\circ}$ , is readily soluble in the usual solvents, and

dissolves in concentrated sulphuric acid, forming a fine blue-coloured solution. When oxidised with chromic acid, it again yields isoindeulucine. A. P.

**Action of Chromium Hexafluoride on Benzoic Acid.** By C. L. JACKSON and G. T. HARTSHORN (*Ber.*, 18, 1993—1995).—Chromium hexafluoride when acting on benzoic acid does not attack the hydroxyl group as was expected, but gives direct substitution derivatives, chromic fluoride,  $\text{Cr}_2\text{F}_6$ , being at the same time formed. As benzene and acetic acid also give fluor-derivatives when similarly treated, it seems probable that this reaction may form a general method for the preparation of fluor-derivatives.

*Difluorobenzoic acid*,  $\text{C}_6\text{H}_3\text{F}_2\cdot\text{COOH}$ , is prepared by the action of chromium hexafluoride on dry benzoic acid, and is purified by fractional precipitation with soda, boiling with water and crystallisation from hot benzene. It resembles benzoic acid in appearance, but sublimes less readily, melts at  $232^\circ$  (uncorr.), is very sparingly soluble in hot water, readily in hot benzene. The *barium* salt,  $(\text{C}_6\text{H}_3\text{F}_2\text{O}_2)_2\text{Ba}$ , and the *calcium* salt,  $(\text{C}_6\text{H}_3\text{F}_2\text{O}_2)_2\text{Ca} + 3\text{H}_2\text{O}$ , are described. A. J. G.

**Action of Phenyl Cyanate on Phenols and Phenol Ethers.** By R. LEUCKART and M. SCHMIDT (*Ber.*, 18, 2338—2341).—Hofmann has shown that phenylic phenylcarbamate is produced by the action of phenyl cyanate on phenol (this Journal, 1871, 392); the author finds that the same reaction occurs in the presence of aluminium chloride. With anisöl and phenyl cyanate the reaction, which only occurs in presence of aluminium chloride, takes quite a different course and yields the anilide of anisic acid; salicylic acid is also formed in small quantity. Phenetoil yields *parethoxybenzanilide*,  $\text{EtO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHPh}$ , crystallising in white needles and melting at  $170^\circ$ . A small quantity of salicylic acid is formed also in this case.

*$\alpha$ -Naphthyl phenylcarbamate*,  $\text{NHPh}\cdot\text{COO}\cdot\text{C}_{10}\text{H}_7$ , is formed by the action of phenyl cyanate on  $\alpha$ -naphthol; it crystallises in slender needles and melts at  $177^\circ$ . The corresponding  *$\beta$ -naphthyl* salt melts at  $230^\circ$ . The naphthyl methyl ethers yield with phenyl cyanate compounds which seem to be the *anilides* of *methoxynaphthoic acids*,  $\text{MeO}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{NHPh}$ . The  $\alpha$ -compound crystallises in slender prisms and melts at  $218^\circ$ , and the anilide from  *$\beta$ -naphthyl methyl ether* melts at  $169^\circ$ .

By the action of phenyl cyanate on thiophen in presence of aluminium chloride, *thiophenic anilide*,  $\text{C}_4\text{SH}_3\cdot\text{CO}\cdot\text{NHPh}$ , seems to be formed. It crystallises in iridescent plates, and melts at  $140^\circ$ .

A. J. G.

**Nitrophenylparaconic Acids.** By H. W. SALOMONSON (*Ber.*, 18, 2153—2156).—*Metanitrophenylparaconic acid*,  $\text{C}_{11}\text{H}_9\text{NO}_6$ , is prepared by heating metanitrobenzaldehyde with sodium succinate and acetic anhydride (equal mols.) at  $125^\circ$ . It is a colourless, crystalline substance which melts at  $171^\circ$ . *Paranitrophenylparaconic acid* is prepared in a similar way, but at a temperature of  $150^\circ$ ; it melts at  $163^\circ$ . Attempts to convert these acids into nitronaphthols failed; acetic

acid at 200° has no action on them, warm sulphuric acid dissolves them without change, whilst hot sulphuric acid carbonises them.

N. H. M.

**Derivatives of Cyanocarbimidoamidobenzoic Acid, and of Dicyanamidobenzoyl.** By P. GRIESS (*Ber.*, 18, 2410—2421).—The author has already described (*Abstr.*, 1879, 321) the above two compounds,  $\text{CN}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$  and  $\text{CN}\cdot\text{C}\begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{CO} \end{smallmatrix} > \text{C}_6\text{H}_4$ , obtained by the action of gaseous cyanogen on cold solutions of metamidobenzoic and anthranilic acids respectively.

I. DERIVATIVES OF CYANOCARBIMIDOAMIDOBENZOIC ACID.—*Carboxamido-carbimidoamidobenzoic acid*,  $\text{NH}_2\cdot\text{CO}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH} + \text{H}_2\text{O}$ , is obtained in the form of its hydrochloride, when a dilute hydrochloric solution of the parent acid is allowed to remain for about a month. The free acid crystallises in small prisms, and has the properties of an amido-acid. It forms salts with bases and with acids, and also platino- and auro-chlorides. When boiled for some time with water it yields *oxalamidoamidobenzoic acid*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , crystallising in small, white, stellate scales, which are very sparingly soluble in the usual neutral solvents. It does not combine with acids; its barium salt crystallises with 5 mols.  $\text{H}_2\text{O}$ . When an aqueous solution of barium cyanocarbimidoamidobenzoate is heated to boiling, ammonia is evolved, and *oxalamidobenzoic acid*,



is formed together with some oxalamidamidobenzoic acid. It forms white scales, tolerably soluble in boiling water, less so in alcohol, and almost insoluble in ether. Its barium salt crystallises with 2 mols.  $\text{H}_2\text{O}$ . In large quantity, this acid is more easily prepared by heating together equal molecular proportions of anhydrous oxalic and metamidobenzoic acids at 180°. When heated at 210°, this acid is converted into the acid  $\text{C}_2\text{O}_2\cdot(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH})_2$ , a white crystalline powder almost insoluble in water, alcohol, and ether. *Dimethylamidodicarbimidoamidobenzoic acid*,  $\text{NMe}_2\cdot\text{C}(\text{NH})\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , is obtained by allowing a solution of the parent acid in 10 per cent. dimethylamine to stand for 4 to 6 days. It forms glistening, white, hexagonal scales soluble in boiling water. It is only a very feeble acid, but its basic properties are more pronounced, and its hydrochloride has the formula  $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_2\cdot\text{HCl}$ . It also forms platino- and auro-chlorides. When its aqueous solution is heated with sodium carbonate at 100°, decomposition takes place according to the equation  $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_2 + 2\text{H}_2\text{O} = \text{NH}_2\cdot\text{C}_2\text{O}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH} + \text{NH}_3 + \text{NHMe}_2$ .

The author has already described (*Abstr.*, 1883, 669) the formation of amidophenylbenzoglycocyanine by the action of an excess of paradiamidobenzene on cyanocarbimidoamidobenzoic acid. If orthodiamidobenzene be employed the reaction is slightly different, *imidophenyl-*

*benzoglycocyanidine*,  $\text{NH}\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH} \end{smallmatrix}$ , being formed. This compound forms hexagonal plates which are almost insoluble in alcohol,

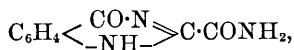
ether, and water, readily soluble in alkalis. It is both a base and an acid, but its basic properties are very feeble, its crystalline chloride being decomposed by cold water. The author considers the constitution of its barium salt to be  $\text{Ba}\left[\text{N}\left\langle\begin{array}{c} \text{C}_6\text{H}_4-\text{CO}\cdot\text{NH} \\ \text{CNH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4 \end{array}\right\rangle\right]_2$ .

*Cyanocarboxamidobenzoic acid*,  $\text{CN}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , is obtained by treating a dilute hydrochloric solution of the parent acid with nitrous acid, according to the equation  $\text{CN}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH} + \text{HNO}_2 = \text{CN}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH} + \text{N}_2 + \text{H}_2\text{O}$ . It forms glistening white scales, soluble in alcohol, almost insoluble in cold water. When boiled with water, it is decomposed into carbonic anhydride and hydrocyanic and carboxamidobenzoic acids. With cold dilute aqueous ammonia, it yields hydrocyanic and uramidobenzoic acids. Methylamine, ethylamine, &c., cause similar decomposition, alkylated uramidobenzoic acids being formed. *Methyluramidobenzoic acid*,

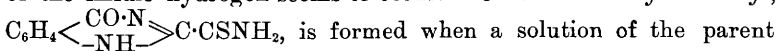


forms white needles, sparingly soluble in water, more easily in alcohol; it yields a silver salt crystallising in scales. *Ethylamidouramidobenzoic acid*,  $\text{NH}_2\cdot\text{C}_2\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , was obtained by the action of ethylenediamine on the parent acid. It crystallises in glistening white columns or prisms easily soluble in boiling water and in alkalis, but not in alkaline carbonates. With acids, it yields crystalline salts and platino- and auro-chlorides. *Hydroxyamidocarbimidocarboxamidobenzoic acid*,  $\text{OH}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , is formed by the solution of cyanocarboxamidobenzoic acid in an equivalent quantity of aqueous hydroxylamine. It yields white needles sparingly soluble in boiling water, and forms an unstable silver salt. The formation is expressed by the equation  $\text{N}(\text{C}_7\text{H}_6\text{O}_2)\cdot\text{CO}\cdot\text{CN} + \text{NH}_2\cdot\text{OH} = \text{NC}_7\text{H}_6\text{O}_2\cdot\text{CO}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{OH}$ , direct union taking place between the CN group and the hydroxylamine. A similar reaction takes place between free cyanogen and hydroxylamine, but the amorphous compound formed is very unstable.

II. DERIVATIVES OF DICYANAMIDOBENZOYL. — Dicyanamidobenzoyl appears to be capable of entering into reaction with a very large number of compounds. *Carboxamidocyanamidobenzoyl*,



is formed when the parent substance is heated with concentrated aqueous ammonia in closed tubes. It forms minute white needles or scales sparingly soluble in water. Although containing no carboxyl-group, it has strongly marked acid properties changing the colour of vegetable dyes, and with bases forming salts in which substitution of the imidic hydrogen seems to occur. *Carbothiamidocyanobenzoyl*,



is formed when a solution of the parent compound in ammonium sulphide is allowed to remain. It crystallises in canary-yellow needles or scales sparingly soluble in water, resembles the previous substance in properties, and is converted into it by continued boiling with dilute ammonia. *Cyanamidobenzoylcarboxylic acid*,



$\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO}\cdot\text{N} \\ \text{---NH---}\end{smallmatrix}\rangle\text{C}\cdot\text{COOH} + \frac{1}{2}\text{H}_2\text{O}$ , is obtained by heating dicyanamido-benzoyl with baryta-water. It forms white scales very sparingly soluble in alcohol and water. It loses its water of crystallisation at  $115^\circ$ . It is stable towards alkalis, and has the properties of a

dibasic acid. The barium salt,  $\begin{array}{c} \text{CO}\cdot\text{N}:\text{C}\cdot\text{CO} \\ | \qquad | \\ \text{C}_6\text{H}_4\text{---N---Ba} \end{array} \rangle \text{O} + 3\text{H}_2\text{O}$ , forms white

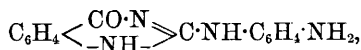
needles which only lose their water of crystallisation at  $205^\circ$ . When boiled with water or acids, or heated by itself, this acid is converted into *carbimidoamidobenzoyl*,  $\text{NH}\langle\begin{smallmatrix}\text{---C}_6\text{H}_4\text{---} \\ \text{C(NH)}\end{smallmatrix}\rangle\text{CO}$ . The latter substance

is a well-characterised base crystallising in white needles, easily soluble in boiling water. It melts at  $214^\circ$ , distils without decomposition, and forms salts and a platinumchloride. It is isomeric with azo-oxindole and imesatin. *Methamidocarbimidocyanamidobenzoyl*,

$\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO}\cdot\text{N} \\ \text{---NH---}\end{smallmatrix}\rangle\text{C}\cdot\text{CNH}\cdot\text{NHMe}$ , crystallises out if a solution of the

parent compound in a 33 per cent. solution of methylamine is allowed to remain for 12 hours. It forms white needles or prisms moderately soluble in boiling water, and yields a *hydrochloride* crystallising in hexagonal scales. When boiled with soda, it is decomposed into carboxamidocyanamidobenzoyl and methylamine. *Phenylbenzoglyco-*

*cycamidinecarboxylic acid*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO}\cdot\text{N} \\ \text{---NH---}\end{smallmatrix}\rangle\text{C}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , which is formed by boiling one part of the parent compound and about two parts of metamidobenzoic acid with much water, crystallises in small snow-white needles almost insoluble in all the usual neutral solvents. It forms two series of salts with one and two equivalents of a base respectively. *Paramidophenylbenzoglycocyamidine*,



is formed if the amidobenzoic acid in the last reaction is replaced by paradiamidobenzene. It yields small, white needles sparingly soluble in boiling water, slightly more so in boiling alcohol. It is isomeric with imidophenylbenzoglycocyamidine described above.

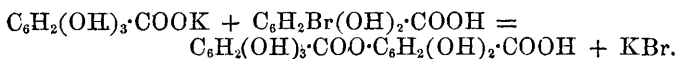
L. T. T.

**Benzenylamidoximecarboxylic Acid.** By G. MÜLLER (*Ber.*, 18, 2485—2486).—*Ethyl paracyanobenzoate*—prepared by Sandmeyer's reaction (this vol., p. 981) from ethyl paramidobenzoate—crystallises in needles which melt at  $54^\circ$ , and are easily soluble in alcohol and ether. With hydroxylamine, it yields *ethyl benzenylamidoximeparacarboxylate*,  $\text{OH}\cdot\text{N}:\text{C}(\text{NH}_2)\cdot\text{C}_6\text{H}_4\cdot\text{COOEt}$ , which forms crystals melting at  $135^\circ$ . The *free acid* melts above  $330^\circ$ .

When meta- or para-cyanobenzoic acid is treated with hydroxylamine, the corresponding benzenylamidoximecarboxylic acid appears to be formed; but the author has not been able to separate them completely from the phthalic acid formed in the reaction, and the excess of cyanobenzoic acid.

L. T. T.

**Synthesis of Tannin.** By B. HUNT (*Chem. News*, **52**, 49).—This synthesis is based on the reaction represented in the following equation:—



The potassium gallate and monobromoprotocatechuic acid are digested together with alcohol on a water-bath for about five hours. A substance can be separated from the product which behaves with many reagents like tannin.

D. A. L.

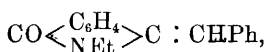
**Methylenephthalide.** By S. GABRIEL (*Ber.*, **18**, 2451—2455).—From the analogy with benzalphthalimidine (next Abstract), the author was inclined to give the formula  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NH} \end{smallmatrix} > \text{C} : \text{CH} \cdot \text{COOH}$  to the phthalylacetamide obtained by him and Michael (*Abstr.*, 1878, 230) by the action of ammonia on phthalylacetic acid. Roser, however, could not obtain a methyl-derivative by substituting methylamine for ammonia in the above reaction, and therefore proposed the formula  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{N} \end{smallmatrix} > \text{C} \cdot \text{CH}_2 \cdot \text{COOH}$  and the name phthalimidylacetic acid for this substance (this vol., p. 159). By treating phthalylacetic acid, moistened with water, with a 33 per cent. solution of methylamine and saturating the liquid with hydrogen chloride—great care being taken to keep everything well cooled—the author has succeeded in obtaining an acid of the formula  $\text{NHMe} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOH}$ , which crystallises in minute prisms melting with partial decomposition at  $145^\circ$ . When dissolved in concentrated sulphuric acid, allowed to remain 24 hours, and then poured into water, it yields *phthalomethimidylacetic acid*,  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NMe} \end{smallmatrix} > \text{C} : \text{CH} \cdot \text{COOH}$ . This substance forms yellowish silky microscopic needles soluble in alcohol, and melting at  $212^\circ$  with decomposition. When heated above its melting point, or with glacial acetic acid, it loses water and carbonic anhydride and forms *methylenephthalomethimidine*,  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NMe} \end{smallmatrix} > \text{C} : \text{CH}_2$ . This substance is volatile in steam, and crystallises in colourless needles, which are easily soluble in alcohol, ether, and chloroform, have a bitter odour, and melt by the warmth of the hand. It is, however, very unstable and, even over sulphuric acid, the crystals soon become sticky and covered with a white sublimate, and lose their odour and volatility. When an aqueous solution is treated with bromine, it yields a derivative,  $\text{C}_{10}\text{H}_{10}\text{NBrO}_2$ . The formation is probably expressed by the equations  $\text{C}_{10}\text{H}_9\text{NO} + \text{Br}_2 + \text{H}_2\text{O} = \text{C}_{10}\text{H}_9\text{NBr}_2\text{O} + \text{H}_2\text{O} = \text{C}_{10}\text{H}_{10}\text{NBrO}_2 + \text{HBr}$ . It forms colourless needles melting at  $125\text{--}126^\circ$ .

The action of ethylamine on phthalylacetic acid is analogous to that of methylamine, and is now being studied.

From these results the author upholds his own formula in preference to that of Roser.

L. T. T.

**Benzylidenephthalide.** By S. GABRIEL (*Ber.*, 18, 2435—2451).—The author finds that the loss of water described as occurring in the reaction of ammonia on benzylidenephthalide (this vol., p. 903) was not due to the primary reaction, but to the dehydrating action of the glacial acetic acid employed as a crystallising agent. In the case of the reaction with ethylamine, alcohol was used as a solvent instead of acetic acid. The primary product in the two cases is therefore quite analogous, namely, the *amide* or *ethylamide*, respectively, of *deoxybenzoïn-carboxylic acid*. Both these compounds lose water when boiled with glacial acetic acid. If the *amide*—crystallising in snow-white needles soluble in alcohol and in boiling water, and melting at 165—166°—is dissolved in boiling glacial acetic acid, and water added until milkiness is produced, the dehydrated substance crystallises out in scales melting at 182—183°. The constitution is therefore  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NH} \end{smallmatrix} > \text{C} : \text{CHPh}$ , and not  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{N} \end{smallmatrix} > \text{C} \cdot \text{CH}_2\text{Ph}$ , as formerly given; the author proposes the name *benzalphthalimidine* as more correct than phthalimidylbenzyl. Ethyl iodide has no action on this substance, even at 200°. The ethylamide, when treated with boiling glacial acetic acid, yields *benzalphthalethimidine*,

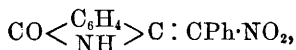


which crystallises in scales easily soluble in carbon bisulphide, light petroleum, chloroform, and ether; softens at 70°, and melts at 75—77°. When treated with concentrated hydrobromic acid, this substance yields white crystals of a bromine-derivative, and with bromine forms a red syrup; but neither of these compounds was obtained in a pure state.

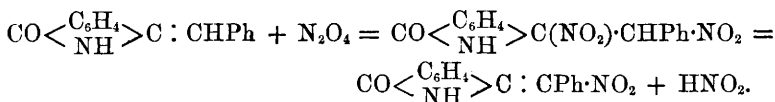
When a mixture of nitric peroxide and oxygen—evolved by the calcination of lead nitrate—was passed into a benzene solution of benzylidene-phthalide, the same dinitrobenzylidene-phthalide was formed as previously (this vol., p. 902) by the action of nitrous acid. The author believes that the reaction in the latter case is due to the nitrous acid first becoming decomposed to nitric peroxide. Stilbene, when similarly treated with nitric peroxide, yields long, colourless needles of *diphenyldinitroethane*,  $\text{C}_2\text{H}_2\text{Ph}_2(\text{NO}_2)_2$ . This compound is sparingly soluble in boiling alcohol, more easily in boiling glacial acetic acid. It melts slowly at 300°, and at the same time turns green, evolves nitrous fumes, and slowly volatilises. Cinnamic acid, under similar circumstances, yields very unstable crystals, which, although they could not be analysed, are, without doubt, *phenyldinitropropionic acid*,  $\text{C}_2\text{H}_2\text{Ph}(\text{NO}_2)_2\text{COOH}$ . When moistened with water, these crystals evolve carbonic anhydride and nitrous fumes, and leave phenylnitroethylene (nitrostyrene),  $\text{CHPh} : \text{CH} \cdot \text{NO}_2$ . The dinitro-acid appears to be more stable at low temperatures, and the author hopes during the winter to be able to prepare it pure for analysis.

The two nitro-derivatives,  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_4$  and  $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_3$ , previously obtained by the action of nitrous acid on benzalphthalimidine, are more readily prepared, in a similar way, from deoxybenzoïn-carboxyl-

amide. Nitric peroxide may be substituted for nitrous acid without altering the products formed. The one, *nitrobenzalphthalimidine*,



already described as benzylnitrophthalidine (*loc. cit.*), is probably formed according to the equations :



When heated with dilute soda solution, this substance takes up the elements of water and is converted into an acid of the formula  $\text{NO}_2 \cdot \text{CPh} : \text{C}(\text{NH}_2) \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , which forms a yellow, crystalline powder melting at  $147-150^\circ$ . It forms crystalline *barium* and *silver* salts. The *ethyl ether*—prepared from the silver salt—forms crystalline granules which melt at  $154-155^\circ$ , and at a slightly higher temperature evolve gas and leave nitrobenzalphthalimidine. The *methyl ether* appears to be still more unstable, as in all attempts to obtain it, the substance formed was nitrobenzalphthalimidine. The free acid is also converted into the latter substance by acetic chloride. A benzene solution of the acid when treated with nitrous acid yields nitrobenzylidenephthalide.

The second nitro-derivative, *hydroxynitrobenzylphthalimidine*,  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NH} \end{smallmatrix} > \text{C}(\text{OH}) \cdot \text{CHPh} \cdot \text{NO}_2$ , forms microscopic, colourless rhombic crystals. When boiled with water or alcohol, or heated above its melting point, it is decomposed into phenylnitromethane,  $\text{CH}_2\text{Ph} \cdot \text{NO}_2$ , and phthalimide. When moistened with acetic chloride, it yields nitrobenzalphthalimidine.

When ortho-deoxybenzoic acid is heated with hydriodic acid and phosphorus at  $190^\circ$ , orthodibenzylcarboxylic acid is formed (*Abstr.*, 1878, 735). This acid, which melts at  $130-131.5^\circ$ , may be more readily obtained by digesting benzylidenephthalide with 1 part of phosphorus and 5 parts of hydriodic acid (b. p.  $127^\circ$ ), treating with water, and extracting the acid from the residue by means of ammonia.

Benzylidenephthalide dibromide (this vol., p. 165), when heated above its melting point, evolves hydrobromic acid, together with a little bromine, and leaves *bromobenzylidenephthalide*. This compound is very unstable, and could not be obtained in a pure state. The specimens obtained melted about  $160^\circ$ . When heated with hydriodic acid and phosphorus, it yields orthodibenzylcarboxylic acid. Bromobenzalphthalimidine,  $\text{C}_{15}\text{H}_{10}\text{NOBr}$  (this vol., p. 903), and nitrobenzalphthalimidine both yield benzylphthalimidine (benzylphthalidine) on reduction.

When nitrobenzylidenephthalide is reduced with hydriodic acid and phosphorus, *isobenzylidenephthalide* (or isobenzalphthalide)  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH} \\ \text{CO} \cdot \text{O} \end{smallmatrix} > \text{CHPh}$ , is formed, isomeric with benzylidenephthalide. This substance crystallises in colourless needles melting at  $90-91^\circ$ .

When it is heated with more hydriodic acid and phosphorus at 200°, orthodibenzylcarboxylic acid is formed. Isobenzalpthalide is insoluble in ammonia or alkali, but when boiled for some time with the latter it takes up the elements of water and becomes converted into *β*-deoxybenzoïnorthocarboxylic acid,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ . This acid crystallises in thin, white needles easily soluble in alcohol and melting at 162—163°. When treated with sodium amalgam, it yields an acid of the formula  $\text{OH} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ . This acid has a great tendency to change into its lactone, and could not be obtained pure in a free state. Its formula was established by the analysis of its silver salt. The lactone, which is very easily formed when the acid is heated above its melting point, crystallises in colourless prisms or needles soluble in alcohol and melting at 89—90°. It is not soluble in ammonia or cold alkali, but when boiled with the latter yields a salt of the acid. When the *β*-deoxy-acid is acted on by hydroxylamine, the compound  $\text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{CH}_2 \\ \text{COO} \cdot \text{N} \end{smallmatrix} \text{CPh}$  is formed, isomeric with that obtained from the  $\alpha$ -acid (this vol., p. 903). It forms reddish needles soluble in alcohol and chloroform, insoluble in ammonia, and melting at 137—139°.

When isobenzalpthalide is heated with alcoholic ammonia at 100°, *isobenzalpthalimidine*,  $\text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{CH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CPh}$ , is obtained. The same substance is produced, though in smaller quantity, by evaporating an ammoniacal solution of the *β*-deoxy-acid. It crystallises in glistening needles or prisms melting at 197°, and moderately soluble in boiling alcohol. When treated with phosphoric chloride, this substance yields the compound  $\text{C}_{15}\text{H}_9\text{NCl}_2$ ; whereas the  $\alpha$ -compound yields a substitution-product which still contains oxygen. The substance  $\text{C}_{15}\text{H}_9\text{NCl}_2$  crystallises in agglomerated needles sparingly soluble in boiling alcohol and melting at 70—75°. It is being further investigated.

L. T. T.

**Constitution of the Sulphinic Acids.** By R. OTTO and A. RÖSSING (*Ber.*, 18, 2493—2509).—In a previous communication (*Abstr.*, 1880, 810) Otto showed that when the alkaline sulphinates are acted upon by haloïd alkyl ethers the resulting compounds are sulphones, and not, as might have been expected, alkyl sulphinates. When attempting to prepare ethylic phenylsulphoformate,  $\text{Ph} \cdot \text{SO} \cdot \text{COOEt}$ , by the action of ethyl chlorocarbonate on sodium benzenesulphinate, the author found that carbonic anhydride was always evolved, and a mixture of the desired ether and ethyl benzenesulphinate was produced; the latter forming always the principal product. The *ethyl benzenesulphinate*,  $\text{Ph} \cdot \text{SO}_2\text{Et}$ , is a very unstable compound, and was not isolated. The mixture forms a mobile, highly refracting liquid, heavier than water. It is insoluble in water, but miscible with the usual organic solvents. The relative proportion of the two products in the mixture was determined by saponification, as well as by analysis. A weighed quantity of the mixture was saponified by boiling with barium hydroxide, when the sulphinat yielded alcohol and barium benzenesulphinate, whilst the ethyl phenylsulphoformate was decomposed into alcohol, and barium

benzenesulphinate and carbonate. The quantity of barium carbonate represented the quantity of the formate originally present. The carbonic anhydride evolved during the reaction of formation was also estimated, and represented the quantity of the sulphinic salt formed. These methods yielded tolerably concordant results. The mixture was found to consist of from 93 to 95 per cent. of the sulphinate and 5 to 7 per cent. of the formate. When heated with water, both salts are resolved into alcohol and acid; but the sulphinic acid is further decomposed into benzenedisulphoxide. When potash is used as a saponifying agent and the product evaporated, the formate undergoes further decomposition into potassium benzenesulphinate and carbonate. Ammonia acts in the same way as a fixed alkali, and does not yield an amide. When treated with sodium amalgam, the ethereal mixture yielded phenyl bisulphide, sodium benzenesulphinate, and ethyl alcohol. When reduced with zinc and hydrochloric acid, phenyl hydrosulphide was formed in considerable quantity.

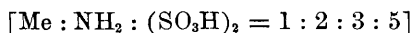
When sodium paratoluenesulphinate is acted on by ethyl chloro-carbonate, the reaction is perfectly analogous to that with the benzenesulphinate. The ethereal mixture produced consisted of about 6 to 7 per cent. of ethyl toluenesulphoformate, and 93 to 94 per cent. of *ethyl toluenesulphinate*,  $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Et}$ . The *paratoluene bisulphide* formed in the decomposition of the sulphinate forms crystals melting at 74–75°, and soluble in alcohol.

By passing hydrogen chloride through an alcoholic solution of benzenesulphinic acid, a liquid was obtained almost wholly soluble in potash. The solution contained only alcohol and potassium benzenesulphinate. The ethereal liquid must therefore have been principally ethyl benzenesulphinate. This salt may be preserved in well-closed bottles, but is very quickly decomposed by exposure to moisture or air. It was not obtained in a pure state. L. T. T.

**Trinitrobenzenesulphonic Acid.** By C. WILLGERODT (*J. pr. Chem.* [2], 32, 117–120).—The *sodium-derivative of trinitrobenzenesulphonic acid*,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{SO}_3\text{Na} + \text{H}_2\text{O}$ , is readily obtained by heating an alcoholic solution of chlorotrinitrobenzene with an excess of hydrogen sodium sulphite for some time at 100°; it forms large, transparent, colourless crystals, is readily soluble in water, but sparingly in alcohol and ether. It loses water of crystallisation at the ordinary temperature, but may be heated to 300° without undergoing fusion or further alteration; when heated on a platinum spatula, it explodes; it is not altered by fuming nitric acid; solutions of the alkalis, however, decompose it into trinitrobenzene and sodium sulphite. The *free sulphonic acid*,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{SO}_3\text{H} + 2\text{H}_2\text{O}$ , may be obtained by treating the sodium salt with concentrated sulphuric acid; it forms large, colourless crystals; on rapidly heating, it first melts at 100°, then becomes solid, and again melts at 185°. It is readily soluble in water, alcohol, and ether, sparingly in chloroform and benzene. A. P.

**Sulphonic and Disulphonic Acids.** By H. LIMPRICHT (*Ber.*, 18, 2172–2192).—In the preparation of these compounds, chlorosul-

phonic acid was used. Toluidinedisulphonic acid,



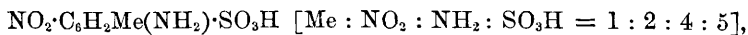
(Trans., 1882, 421), was prepared and examined. Several salts are described. The *diazo-compound*,  $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_5 \cdot \text{SO}_3\text{N}$ , forms yellow, microscopic needles; when boiled with water it yields *cresoldisulphonic acid*, readily soluble in water and in alcohol. Salts of both these compounds are described. When the diazo-compound is boiled with absolute alcohol under pressure, it yields *ethoxytoluenedisulphonic acid*,  $\text{EtO} \cdot \text{C}_6\text{H}_5 \cdot (\text{SO}_3\text{H})_2$ . A *barium salt* with 2 mols.  $\text{H}_2\text{O}$  is described. *Bromotoluenedisulphonic acid* was obtained from the diazo-derivative. The *chloride* forms colourless prisms melting at  $90^\circ$ ; the *amide* melts at  $236\text{--}238^\circ$ . The *potassium salt* (with  $2\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ ) of toluenedisulphonic acid is described. The *chloride* of this acid forms long, colourless prisms which melt at  $132^\circ$ ; the *amide* crystallises in small, lustrous plates melting above  $240^\circ$ .

*Paratoluidinemetadisulphonic acid*,  $\text{C}_6\text{H}_4\text{Me}(\text{SO}_3\text{H})_2 \cdot \text{NH}_2 + 2\text{H}_2\text{O}$ , is prepared from paratoluidinemetasulphonic acid. It is readily soluble in water, less so in alcohol. At  $200^\circ$  (or with water at  $140^\circ$ ), it decomposes into the monosulphonic acid and sulphuric acid. Various salts were prepared. The diazo-compound and its *potassium*, *barium*, and *lead salts* are described. These salts when boiled with water yield salts of *cresoldisulphonic acid*. Nitrous acid acts on toluidinedisulphonic acid with formation of *dinitrocresol*,  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$ ; it forms yellow needles readily soluble in alcohol, sparingly in water, and melts at  $82\cdot5^\circ$ . Several salts were prepared. *Bromotoluenedisulphonic acid*,  $\text{C}_6\text{H}_4\text{Br}(\text{SO}_3\text{H})_2$ , obtained from the diazo-compound, forms a brownish mass of crystals. The *potassium* (with 1 mol.  $\text{H}_2\text{O}$ ) and *barium* (with 6 mols.  $\text{H}_2\text{O}$ ) salts are described. The *chloride*,  $\text{C}_6\text{H}_4\text{Br}(\text{SO}_2\text{Cl})_2$ , melts at  $133^\circ$ ; the *amide* forms long prisms melting above  $240^\circ$ . *Iodotoluenedisulphonic acid*,  $\text{C}_6\text{H}_4\text{I}(\text{SO}_3\text{H})_2$ , forms long, white needles readily soluble in water and alcohol; several salts are described. The *chloride* forms white prisms very sparingly soluble in ether, and melting at  $143^\circ$ . The *amide* melts at  $130\text{--}132^\circ$ .

*Paratoluidinedisulphonic acid*,  $\text{C}_6\text{H}_4\text{Me}(\text{SO}_3\text{H})_2 \cdot \text{NH}_2 + 2\frac{1}{2}\text{H}_2\text{O}$ , is obtained from paratoluidineorthosulphonic acid; it forms colourless needles readily soluble in water, less soluble in alcohol. At  $290^\circ$  it becomes black, and is resolved into the monosulphonic acid and sulphuric acid. Several salts of the acid are described.

*Orthotoluidineparasulphonic acid*,  $\text{C}_6\text{H}_4\text{Me}(\text{SO}_3\text{H})_2 \cdot \text{NH}_2 + 2\text{H}_2\text{O}$ , prepared from orthotoluidineparasulphonic acid, crystallises in well-formed, microscopic prisms which decompose at  $290\text{--}300^\circ$  into sulphuric acid and orthotoluidinesulphonic acid. The *barium* and *calcium salts* (each with 2 mols.  $\text{H}_2\text{O}$ ) and the *diazo-derivative* are described.

*Nitrotoluidinesulphonic acid*,



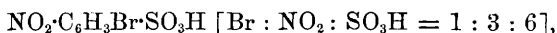
is prepared by heating nitrotoluidine with chlorosulphonic acid at  $160^\circ$ . It forms bright yellow needles sparingly soluble in alcohol and cold water. The *potassium* (with 1 mol.  $\text{H}_2\text{O}$ ), *barium* (with 4 and 1 mol.

H<sub>2</sub>O), and the *lead* (with ? 3½ H<sub>2</sub>O) salts are described. The *diazo-derivative* forms a reddish-brown crystalline powder, insoluble in cold water and boiling alcohol. When heated with absolute alcohol at 100°, it yields *nitrotoluenesulphonic acid*, NO<sub>2</sub>·C<sub>7</sub>H<sub>6</sub>·SO<sub>3</sub>H. The *chloride* of this acid melts at 50°; the *amide* melts at 133·5°. When the diazo-compound is treated with sodium dissolved in absolute alcohol, it yields *ethoxynitrotoluenesulphonic acid*, NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>Me(OEt)·SO<sub>3</sub>H; when heated with hydriodic acid, it yields *iodotoluidinesulphonic acid*, NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>MeI·SO<sub>3</sub>H + H<sub>2</sub>O, which forms slender, lustrous needles soluble in hot water. *Tolylenediaminesulphonic acid*,



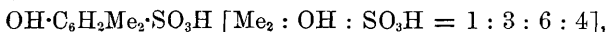
is prepared by reducing nitrotoluidinesulphonic acid; it forms hard, lustrous prisms. The *hydrochloride* and *hydrobromide* are described. The *potassium* (with 1 mol. H<sub>2</sub>O) and the *barium* (with 5½ mols. H<sub>2</sub>O) salts were prepared.

*Nitrobromobenzenesulphonic acid*,



is prepared from the *diazo-derivative* of nitranilinesulphonic acid (Abstr., 1880, 394); the *chloride* forms large, yellow plates melting at 75°; the *amide* melts at 166°.

*Xylenolsulphonic acid*,



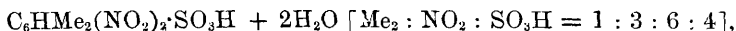
is obtained by boiling the *diazo-derivative* from xyridenesulphonic acid (Abstr., 1883, 593); the *potassium*, *barium* (with 1 mol. H<sub>2</sub>O), and *lead* (with 2 mols. H<sub>2</sub>O) salts are described. *Ethoxyxylenesulphonic acid*, EtO·C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>·SO<sub>3</sub>H, obtained from the same diazo-compound by the action of absolute alcohol, forms microscopic colourless plates very readily soluble in water and in alcohol. The *barium salt* (with 3 mols. H<sub>2</sub>O) is described.

*Nitro-xylidinesulphonic acid*, NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>(NH<sub>2</sub>)·SO<sub>3</sub>H, forms colourless, voluminous crystals very sparingly soluble in hot water. Several salts are described. The *diazo-derivative* forms a white amorphous powder very sparingly soluble in water. *Nitroxxylenolsulphonic acid*, NO<sub>2</sub>·C<sub>6</sub>HMe<sub>2</sub>(OH)·SO<sub>3</sub>H [Me<sub>2</sub> : OH : SO<sub>3</sub>H = 1 : 3 : 6 : 4], crystallises in yellow needles. The *barium* and *lead salts* (each with 3 mols. H<sub>2</sub>O) are described.

*Bromonitro-xylenesulphonic acid* [Me<sub>2</sub> : Br : SO<sub>3</sub>H = 1 : 3 : 6 : 4], crystallises in long, colourless, rhombic plates readily soluble in water and alcohol. The *potassium* and *barium salts* are prepared. *Ethoxy-nitro-xylenesulphonic acid*, NO<sub>2</sub>·C<sub>6</sub>HMe<sub>2</sub>(OEt)·SO<sub>3</sub>H, together with its *potassium* and *barium salts*, are described. *Diamido-xylenesulphonic acid*, C<sub>6</sub>HMe<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub>·SO<sub>3</sub>H, forms short prisms sparingly soluble in water. The *hydrochloride* and some salts were prepared.

*Nitrosulphotoluic acid*, NO<sub>2</sub>·C<sub>7</sub>H<sub>5</sub>(SO<sub>3</sub>H)·COOH, is obtained in small quantities by oxidising nitroxxylenesulphonic acid. The *potassium salt* (with ½ mol. H<sub>2</sub>O) forms lustrous needles.

An acid of the formula





is obtained by the oxidation of xylenesulphonic acid; it forms a readily soluble mass of needles. The *potassium, barium* (with 3 mols.  $\text{H}_2\text{O}$ ), and *lead* (with  $3\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ ) salts are described. The *chloride* crystallises in yellow prisms melting at  $123^\circ$ ; the *amide* forms white, lustrous prisms which melt at  $193^\circ$ .  
N. H. M.

### Action of Phenol and Sulphuric Acid on Hippuric Acid.

II. By J. ZEHENTER (*Monatsh. Chem.*, **6**, 523—530).—*Phenylglycocine-sulphonic acid*,  $\text{C}_8\text{H}_{11}\text{O}_6\text{NS}$ , obtained by the action of sulphuric acid and phenol on hippuric acid (this vol., p. 55), is not attacked by a boiling solution of potassium hydroxide, but is completely decomposed by fusion with solid potash. Attempts to remove the sulphonic group by this reagent were unsuccessful. The acid is decomposed by the action of dilute hydrochloric acid at  $140^\circ$ , yielding phenol, glycocine, and sulphuric acid. The sulphonic group is also removed by nitric acid, and at the same time a trinitrophenol is produced, which differs in some respects from the known trinitrophenols. Its melting point varies between  $90^\circ$  and  $104^\circ$ . The potassium salt resembles potassium picrate, but the naphthalene compound melts at  $138^\circ$ , whilst naphthalene picrate melts at  $149^\circ$ .

The crystalline compound obtained by the action of aqua regia on phenylglycocinesulphonic acid (*loc. cit.*), is orthochlorometadinitrophenol.  
W. C. W.

### Derivatives of Carbostryl and of Hydroxypyridine. By

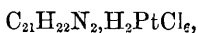
A. FEER and W. KÖNIGS (*Ber.*, **18**, 2394—2400).—*Methylcarbostryl-sulphonic acid*,  $\text{C}_{10}\text{H}_8\text{ON}\cdot\text{SO}_3\text{H}$ , is prepared by adding methylcarbostryl sulphate to fuming sulphuric acid, and then pouring the mixture on to ice. It crystallises in white needles. The silver salt,  $\text{C}_{10}\text{H}_8\text{NSO}_4\text{Ag}$ , crystallises in white needles. The acid yields a trichloroquinoline when treated with phosphoric chloride. When oxidised with dilute aqueous permanganate, an acid is obtained forming clear brown crystals readily soluble in water. It contains sulphur and nitrogen.

*Nitromethylcarbostryl*,  $\text{C}_{10}\text{H}_8\text{ON}\cdot\text{NO}_2$ , is prepared by treating the silver derivative of nitrocarbostryl with methyl iodide; it crystallises in long needles, melts at  $181^\circ$ , sublimes when further heated, is sparingly soluble in alcohol, soluble in ether, benzene, and chloroform, readily soluble in concentrated acids, but reprecipitated on slight dilution.

*Amidomethylcarbostryl*,  $\text{C}_{10}\text{H}_8\text{ON}\cdot\text{NH}_2$ , is prepared by reducing the nitro-compound with stannous chloride. It crystallises in silvery plates, melts at  $103^\circ$ , and is readily soluble in the ordinary solvents, the solutions showing a blue fluorescence. When heated with dilute hydrochloric acid at  $120^\circ$ , it yields amidocarbostryl. When oxidised with dilute aqueous permanganate, it yields a *methoxyquinolinic acid*,  $\text{MeO}\cdot\text{C}_8\text{NH}_2(\text{COOH})_2$  [ $\text{MeO} : \text{COOH} : \text{COOH} = 2 : 5 : 6$ ]. This crystallises in long needles, melts at  $140^\circ$  with decomposition, is insoluble in benzene, chloroform and acetic acid, readily soluble in water, alcohol and acetic acid. The acid silver salt,  $\text{C}_8\text{H}_6\text{NO}_5\text{Ag} + \text{C}_8\text{H}_7\text{NO}_6$ , crys-

tallises in white needles. When heated with dilute hydrochloric acid at 120°, it yields a hydroxyquinolinic acid which seems to be identical with that described by Königs and Körner. A. J. G.

**Derivatives of Triphenylmethane.** By C. ULLMANN (*Ber.*, 18, 2094).—By heating a mixture of paratoluidine, paratoluidide hydrochloride, and benzaldehyde for several hours at 120°, a *diamido-dimethyltriphenylmethane* is obtained, which crystallises from benzene in lustrous, white needles of the formula  $2\text{CHPh}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2 + \text{C}_6\text{H}_6$ . This loses its benzene of crystallisation at 120°, and melts at 185° (uncorr.). Its salts crystallise well. The platinochloride,



forms a yellow crystalline powder. An isomeric compound is obtained in a similar manner from orthotoluidine.

The known diamidotriphenylmethane can be obtained by heating a mixture of benzyldeneaniline with aniline hydrochloride, or of benzaldehyde with aniline and aniline hydrochloride. A. J. G.

**Derivatives of Benzophenone.** By R. GEIGY and W. KÖNIGS (*Ber.*, 18, 2400—2407).—Metanitrobenzophenone can be obtained by heating metanitrobenzoic chloride with benzene and aluminium chloride (compare Becker, *Abstr.*, 1883, 203). When reduced with stannous chloride, it yields *metamidobenzophenone*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ ; this crystallises in interlaced, yellow needles, melts at 87°, is sparingly soluble in water, readily in alcohol and ether. The hydrochloride crystallises in colourless needles and melts at 187°; other salts are described.

*Orthonitrobenzophenone*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ , cannot be prepared by heating together a mixture of orthonitrobenzoic chloride, benzene, and aluminium chloride, but is formed on oxidising orthonitrotriphenylmethane. It forms colourless crystals, melts at 105°, and is rather sparingly soluble in absolute alcohol.

*Orthamidobenzophenone*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ , is obtained by reducing the nitro-compound with tin and hydrochloric acid; it crystallises in yellow, shimmering plates or in lustrous, thick, yellow crystals, melts at 105—106°, and is readily soluble in dilute acids, alcohol, and ether. The authors point out that as neither the ortho- nor meta-amidobenzophenones agree in melting point with Doebner's amidobenzophenone (benzoaniline) prepared from phthalylbenzoanilide, his disputed assumption that that substance is a para-compound was in all probability correct.

*Phenyl quinaldyl ketone*,  $\text{C}_9\text{NH}_5\text{Me}\cdot\text{COPh}$  [ $\text{COPh} : \text{Me} = 1 : 2'$ ], is obtained when orthamidobenzophenone is heated in a reflux apparatus with paraldehyde and dilute sulphuric acid. It crystallises in interlaced, colourless needles, melts at 107—108°, and is soluble in alcohol and ether.

*Phenylquinaldine*,  $\text{C}_9\text{NH}_5\text{MePh}$  [ $\text{Me} : \text{Ph} = 2' : 4'$ ], is obtained by boiling 5 grams of orthamidobenzophenone, 40 c.c. of absolute alcohol, 15 c.c. of pure acetone, and 12 c.c. of aqueous potash (1 : 2) in a reflux apparatus for 5—6 hours. It forms colourless crystals,

melts at 98—99°, is nearly insoluble in water, readily soluble in alcohol, ether, and dilute acids, the acid solutions showing a blue fluorescence. The sulphate, chromate, and platinochloride are described. When treated with phthalic anhydride and zinc chloride, it yields a phthalone crystallising in golden-yellow needles and melting at 270°.

Orthonitrodiphenylmethane is most conveniently prepared by the action of aluminium chloride on a mixture of benzene and orthonitrobenzyl chloride.  
A. J. G.

**Benzoylacetone.** By E. FISCHER and C. BÜLOW (*Ber.*, 18, 2131—2138; comp. Abstr., 1884, 59).—Benzoylacetone is best obtained by boiling 50 grams of *pure* ethylic benzoylacetate with 600 grams of water for two hours, allowing it to get quite cold, and again boiling for 2½ hours. The product is then distilled with steam, and that part of the distillate which yields crystals at 0° is shaken with a 1 per cent. soda solution. This is then filtered from the acetophenone which is present, and treated with carbonic anhydride to precipitate the ketone, which separates in slender white needles. The compound dissolves sparingly in hydrochloric acid, readily in warm nitric acid without change.

*Dibenzoylacetone*,  $C_{17}H_{14}O_3$ , is prepared by acting on sodium benzoylacetone with benzoic chloride; it is almost insoluble in water, rather readily soluble in alcohol and in ether, and melts at 102°. It is dissolved with decomposition by alkalis; sodium does not act on it.

*Dibenzoyldiacetylene*,  $C_{20}H_{18}O_4$ , is formed by the action of iodine on sodium benzoylacetone. It crystallises in needles melting at 173—175°, and is insoluble in water and alkalis, sparingly soluble in ether, but more readily in hot alcohol.

*Benzoylacetoneamine*,  $C_{10}H_{11}NO$ , prepared by heating a solution of benzoylacetone in concentrated ammonia at 120°, forms fine quadratic crystals which melt at 143°. It dissolves in cold dilute mineral acids unchanged, but is decomposed into ammonia and benzoylacetone when heated with them. The imido-group has therefore taken the place of an oxygen-atom in benzoylacetone.

The base obtained by Fischer and Kuzel (*loc. cit.*) by acting on benzoylacetone with phenylhydrazine is now shown to be methyl-diphenylpyrrazene,  $C_{16}H_{14}N_2$ . An intermediate product is formed, which, however, is so unstable that it could not be examined. The base was already prepared by Knorr and Blank (*this vol.*, p. 556). Orthonitrobenzoylacetone gives a similar product with phenylhydrazine, identical with a compound prepared by Gevekoht (*Abstr.*, 1884, 445), who, however, considered it to be a compound of 1 mol. of the diketone with 2 mols. of phenylhydrazine. It is more probably an orthonitro-derivative of methyl-diphenylpyrrazene.

*Phenylacetylacetone*,  $CH_3Ph \cdot CO \cdot CH_2Ac$ , is prepared in a manner similar to the benzoyl-derivative. It dissolves rather readily in hot water, easily in alcohol, chloroform, ether, and benzene, and boils at 266—269°. It dissolves readily in cold dilute alkalis and in concentrated mineral acids, and is decomposed by the latter when boiled with them. With phenylhydrazine, it yields *methylphenylbenzyl-*

pyrrazene,  $C_{17}H_{16}N_2$ , readily soluble in dilute hydrochloric acid, from which solution it is precipitated by alkalis or ammonia.

N. H. M.

**Synthesis of Ketonic Acids from Aldehydes and Ethyl Diazoacetate.** By E. BUCHNER and T. CURTIUS (*Ber.*, 18, 2371—2377).—When benzaldehyde and ethyl diazoacetate (equal mols.) are mixed with an equal volume of toluene and heated in a reflux apparatus as long as nitrogen is evolved, ethyl benzoylacetate is formed. If, however, benzaldehyde (3 mols.) and an alkyl diazoacetate (2 mols.) are heated without addition of toluene, then a benzaldibenzoylacetate,  $CHPh(CH\dot{B}z\cdot COOR)_2$ , is formed.

*Ethyl benzaldibenzoylacetate*,  $CHPh(CH\dot{B}z\cdot COOEt)_2$ , crystallises in tables, melts at  $103^\circ$ , is insoluble in water, readily soluble in hot alcohol and in ether. The *sodium-derivative*,  $CHPh(CNa\dot{B}z\cdot COOEt)_2$ , is precipitated after some time in colourless needles on adding sodium ethoxide to an ethereal solution of the ethyl salt. The *methyl salt*,  $C_{27}H_{24}O_6$ , crystallises in prisms and melts at  $113^\circ$ ; its *sodium-derivative* crystallises in tufts of white needles.

The *free acid* seems to be formed on acidifying the sodium-derivatives of either the methyl or ethyl salts; it crystallises in prisms and melts at  $130^\circ$ . The barium and silver salts are described.

A. J. G.

**Nitrosophenols.** By H. GOLDSCHMIDT and H. SCHMID (*Ber.*, 18, 2224—2227).—Methylhydroxylamine hydrochloride acts on  $\beta$ -naphthaquinone with formation of methyl  $\beta$ -nitroso- $\alpha$ -naphthol; this confirms the view put forward by Goldschmidt (this vol., p. 775) that the constitution of the latter compound is  $O:C_{10}H_8:NO.Me$ .

By the action of methylhydroxylamine hydrochloride on  $\alpha$ -naphthaquinone, a compound of the formula  $C_{11}H_9NO_2$  is formed, which, when reduced, yields  $\alpha$ -amido- $\alpha$ -naphthol. The identity of this substance with methylic  $\alpha$ -nitroso- $\alpha$ -naphthol (comp. this vol., p. 169) is not yet established; its melting point is lower than that ascribed by Ilinski to that compound (*loc. cit.*).

N. H. M.

**$\alpha$ - $\beta$ -Diamidonaphthalene, and the Action of Diazo-compounds on  $\beta$ -Naphthylamine.** By T. A. LAWSON (*Ber.*, 18, 2422—2427).—This is a continuation of the author's previous work on this subject (this vol., p. 802). When amyl nitrite acts on  $\beta$ -naphthylamine,  $\beta$ -diazonaphthalene- $\beta$ -naphthylamine,  $C_{10}H_7\cdot N_2\cdot NH\cdot C_{10}H_7$  (identical with the compound produced by the action of  $\beta$ -diazonaphthylamine on  $\beta$ -naphthylamine), is formed. It crystallises in agglomerated needles melting at  $143^\circ$ , is easily soluble in benzene and glacial acetic acid, insoluble in water, and is decomposed, with evolution of nitrogen, when boiled with 20 per cent. sulphuric acid. It resembles diazobenzene- $\beta$ -naphthylamine in properties. Its *acetyl-derivative* is easily soluble in benzene, sparingly so in alcohol and light petroleum, crystallises in prisms, and melts at  $218^\circ$ . The *benzoyl-derivative* forms red needles melting at  $177^\circ$ , and easily soluble in benzene, sparingly in alcohol and light petroleum. When this diazo-compound is subjected to reduction,  $\beta$ -naphthylamine and  $\alpha$ - $\beta$ -diamidonaphthalene are formed. All attempts to isolate the amidoazo-com-

pound, which is undoubtedly formed as an intermediate product during the reduction, proved fruitless. All the members of the above class of diazo-amido-compounds are easily decomposed by bromine, nitrogen being evolved, and brominated phenols and  $\alpha$ -dibromo- $\beta$ -naphthylamine formed. The latter compound is easily soluble in benzene and alcohol, sparingly in water. It crystallises in long, colourless needles, which melt at  $121^\circ$ . Its *acetyl*-derivative melts at  $208^\circ$ . The diamidonaphthalene already mentioned is identical with that which Griess believes to be ortho- $\alpha$ - $\beta$ -diamidonaphthalene. A careful investigation of this substance by the author, by the help of Ladenburg's, Lellmann's, and Hinsberg's reactions, has confirmed this view. With phenanthraquinone, it yields *phenanthrenenaphthaquinoxaline*,  $C_{12}H_8 : (CN)_2 : C_{10}H_6$ , which forms minute yellow crystals sparingly soluble in benzene, melting at  $273^\circ$ , and giving a red coloration with hydrochloric acid. With benzil, the diamine forms *diphenylnaphthaquinoxaline*,  $C_{10}H_6 : (CN \cdot Ph)_2$ . The latter crystallises in light-brown scales which melt at  $147^\circ$  and are easily soluble in alcohol and ether.

The constitution of this class of so-called diazo-amido-compounds from  $\beta$ -naphthylamine has still to be determined. Attempts to produce similar compounds from ortho-xylylene and pseudocumidine proved unavailing; the compounds formed were true diazo-amido-derivatives, and yielded the corresponding hydrazines on reduction.

L. T. T.

**Derivatives of Naphthalene.** By A. PRAGER (*Ber.*, **18**, 2158—2165).—Bromonitracetonaphthalide was prepared by adding, first, a solution of 85 grams of bromine in 70 grams of 30 per cent. soda, then 75 grams of 26 per cent. hydrochloric acid, to 100 grams of  $\alpha$ -acetonaphthalide mixed with water, rubbing well all the time to prevent the formation of lumps. The liquid portion was then removed, and the residue, after being well washed with water, was crystallised from alcohol. The yield is excellent.

*Bromethenylnaphthalenediamine*,  $C_{12}H_9N_2Br$ , is prepared from the above compound by reduction with zinc chloride; it dissolves readily in alcohol and ether, is insoluble in water, and melts at  $229^\circ$ . The *hydrochloride* crystallises from hot alcohol in needles. The compound is an anhydro-base, and can therefore only be formed from a bromonitracetonaphthalide of the constitution  $[NHAc : NO_2 = 1 : 2]$ . The ethenyl group cannot be removed either by boiling potash or sulphuric acid, or by hydrochloric acid at  $210^\circ$ . Sodium amalgam acts on it with formation of *ethenylnaphthalenediamine*,  $C_{12}H_{10}N_2$ . The *hydrochloride* and *nitrate* of the latter compound are described.

*Nitrobromethenylnaphthylenediamine*,  $C_{12}H_9N_3O_2Br$ , was obtained from bromethenylnaphthylenediamine; it forms dark-yellow needles melting at  $242^\circ$ . The *nitrate* and *sulphate* are described. The nitro-group is not in the same ring as the other substituted radicles. Tribromonaphthalene, identical with that obtained by Meldola (*Trans.*, 1883, 4), was prepared by the action of hydrobromic acid on bromonitronaphthalene; its constitution is  $[Br_3 = 1 : 2 \text{ or } 3 : 4]$ . When nitrated, it yields dinitrotribromonaphthalene. N. H. M.

**$\alpha$ -Diamidophenanthraquinol.** By S. KLEEMANN and W. WENSE (*Ber.*, **18**, 2168—2169).—*Diamidophenanthraquinol hydrochloride*,  $C_{14}H_6(NH_2, HCl)_2(OH)_2 + 3H_2O$ , is prepared from Graebe's  $\alpha$ -dinitrophenanthraquinone by the action of stannous chloride. It forms long, lustrous needles, which lose their water of crystallisation and some hydrochloric acid at  $100^\circ$ . When an alcoholic solution is shaken with ether and some ammonia, it acquires a stable, splendid blue colour. When a solution of the salt is exposed to air, dark-violet needles of  $\alpha$ -diamidophenanthraquinone,  $C_{14}H_{10}N_2O_2$ , separate; the change is accelerated by the addition of ferric chloride or potassium dichromate. *Tetracetyl- $\alpha$ -diamidophenanthraquinol*,  $C_{14}H_6(NHAc)_2(OAc)_2$ , forms colourless, slender needles, sparingly soluble in alcohol and glacial acetic acid. It does not melt at  $300^\circ$ . N. H. M.

**Isomeric Dihydroxydimethylantraquinones.** By S. v. KOSTANECKI and S. NIEMENTOWSKI (*Ber.*, **18**, 2138—2141).—*Acetyl-dihydroxydimethylanthrarufin*,  $C_{16}H_{10}O_2Ac_2$ , is prepared by boiling dihydroxydimethylanthrarufin (comp. this vol., p. 531) with acetic anhydride and sodium acetate; it crystallises in tufts of yellow plates melting at  $236$ — $237^\circ$ . When dimethylanthrarufin is distilled with zinc-dust, it yields a product probably identical with Brunner's dimethylanthracene.

The soluble portion of the product obtained by the action of sulphuric acid on hydroxytoluic acid (*loc. cit.*) was found to contain dimethylanthraflavic acid and dimethylbenzodihydroxyanthraquinone.

*Dimethylanthraflavic acid*,  $C_{14}H_6Me_2O_4$ , sublimes in yellow needles, melts above  $360^\circ$ , and is sparingly soluble in alcohol and glacial acetic acid, insoluble in benzene. Its *acetyl*-derivative forms pale-yellow needles which melt at  $223^\circ$ .

*Dimethylbenzodihydroxyanthraquinone*,  $C_{14}H_6Me_2O_4$ , melts at  $213^\circ$ ; it is soluble in glacial acetic acid, less so in alcohol and benzene. The solution in alkali is gold-coloured. Its *acetyl*-derivative melts at  $188^\circ$ . N. H. M.

**Constitution of Alkylhydroxanthranols.** By C. LIEBERMANN (*Ber.*, **18**, 2150—2152).—These compounds (comp. Abstr., 1882, 860) do not yield nitrogenous derivatives with hydroxylamine or phenyl-

hydrazine. The constitution  $EtC \begin{array}{c} \diagup C_6H_4 \\ \diagdown O \\ \diagup C_6H_4 \end{array} C \cdot OH$  is now proposed for

the ethyl-derivative of hydroxanthrol, whilst for hydroxanthrol itself, which behaves differently from the alkyl derivatives in dissolving in alkali (it forms a deep-blue solution), the constitutional formulæ  $CO \begin{array}{c} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} CH \cdot OH$  or  $HO \cdot C \begin{array}{c} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} C \cdot OH$  are suggested.

N. H. M.

**Benzylhydroxanthranol.** By L. LEVI (*Ber.*, **18**, 2152—2153).—*Benzylhydroxanthranol*,  $C_{21}H_{16}O_2$ , is prepared by acting on a boiling mixture of 5 parts of anthraquinone, 5 parts of zinc-dust, 7.5 parts of potash, and 100 parts of water with 5 parts of benzyl bromide. It dissolves readily in alcohol, benzene, and glacial acetic acid, and melts

at 146°. When heated with sulphuric acid at 70°, it acquires a violet-red colour, and is converted into *dehydrobenzylhydroxanthranol*,  $C_{21}H_{14}O$ . This is readily soluble in alcohol and glacial acetic acid, and crystallises in long, yellow needles which melt at 127°. Chromic acid converts it into anthraquinone. The author intends investigating the substance.

N. H. M.

**Campholenic Acid.** By R. ZÜRRER (*Ber.*, **18**, 2228—2229).—As further evidence that the campholenic acid prepared by the author (*Abstr.*, 1884, 1364) is identical with Kachler and Spitzer's hydroxycamphor, (*comp. this vol.*, p. 173), campholenic acid from camphoroxime was nitrated, and a nitrohydroxycamphor obtained, identical with that obtained from hydroxycamphor. *Calcium campholenate*,  $Ca(C_{10}H_{15}O_2)_2$ , forms long, lustrous, white needles, sparingly soluble in water. When distilled alone, or with calcium formate, it yields nothing but hydrocarbons.

N. H. M.

**Sylvic and Pimaric Acids.** By S. HALLER (*Ber.*, **18**, 2165—2168).—The author has repeated the experiments made by Liebermann (*Abstr.*, 1884, 1364) to determine whether the two acids are identical. Sylvic acid melts at 161—162°, and pimaric acid at 149°. When reduced, both acids yield the same inactive hydrocarbon; the analytical results obtained agree with those of Liebermann (*loc. cit.*). The author intends examining the optical properties of the acids.

N. H. M.

**The Gum Ferment.** By J. WIESNER (*Monatsh. Chem.*, **6**, 592—619).—Gum arabic contains a diastatic ferment which is also met with in nearly all the different varieties of gum, in mucilage, in linseed, &c., and in those plant tissues in which the cellulose changes to gum. This ferment is incapable of decomposing glucosides. It does not convert proteids into peptones, nor has it an "inverting" action. It converts starch into dextrin and arabin or bassorin. The gum ferment may be detected by boiling the substance with orcinol and strong hydrochloric acid. A red coloration is produced; the liquid then turns violet, and deposits a blue precipitate which is soluble in alcohol. The ferment is decomposed by boiling in water for one hour and a half. The presence of this ferment interferes with the conversion of starch into sugar by bacteria or by diastase. The conversion of cellulose into gum or mucilage in living plants appears to be due to this substance.

W. C. W.

**Chlorophyll.** By E. SCHUNCK (*Proc. Roy. Soc.*, **38**, 336—340).—It has long been known that the action of acids on chlorophyll produces both a change of colour and of absorption spectrum. Thus, if hydrogen chloride be passed into an alcoholic solution of this substance a dark-green precipitate is produced, which consists, according to Fremy's observations, of two colouring matters, phyllocyanin and phylloxanthin. These are best separated by solution in ether and the gradual addition of concentrated hydrochloric acid, which separates the liquid into two layers, a lower, blue, containing phyllocyanin, an upper, yellowish-green, containing phylloxanthin. In this paper

the properties and reactions of the former are described. It forms microscopic crystals generally opaque and of an indigo colour, but olive-green and translucent when very thin. It may be heated to 160° without decomposition; it contains nitrogen, but no sulphur; is insoluble in water and petroleum, but soluble in alcohol, ether, and chloroform, a very minute trace imparting an intense colour to the solvent. Very dilute solutions give the absorption spectrum of the so-called "acid chlorophyll," consisting of five bands, three dark, one of moderate intensity, the fifth very faint. Phyllocyanin is far more permanent than chlorophyll; with oxidising agents it yields yellow amorphous products; with bromine, a grass-green solution. It dissolves in concentrated acid, yielding dark-blue solutions, showing spectra different from that of the original substance; it dissolves also in the alkalis, and the solution gives green precipitates with various metallic salts. When heated with aniline, it forms several products, one of which is colourless and crystalline, whilst another, possibly an anilide, gives a red solution with a characteristic absorption spectrum. Phyllocyanin apparently acts as a feeble base, uniting with strong acids to form unstable combinations; when dissolved in acetic acid in presence of various metallic oxides, compounds are formed containing the elements of the acid, the base, and phyllocyanin. These compounds are more or less soluble in alcohol, ether, and chloroform, but insoluble in water, with the exception of the manganese compound. The solutions are not precipitated by hydrogen sulphide. They also dissolve in dilute alkalis but are reprecipitated on addition of acetic acid. These results probably explain the observations of Church and of Tschirch, who noticed that a chlorophyll solution which had become brown on standing, gave a green solution when treated with zinc powder.

V. H. V.

**Entero-chlorophyll.** By C. A. MACMUNN (*Proc. Roy. Soc.*, **38**, 319—322).—As a continuation of the author's researches on entero-chlorophyll (*Abstr.*, 1883, 1159, and 1884, 194), it is here shown that it is not due to symbiotic algæ, nor to an intermediate food product from the intercellular digestion of plant chlorophyll, but differs from chlorophyll both from plants and the *Spongilla*. This is evidenced by the replacement of the single absorption band in the red of ordinary chlorophyll by two bands, and also by a red fluorescence of the solution. Both plant- and entero-chlorophyll yield on hydrolysis a chlorophyll-green and a chlorophyll-yellow, the former crystallising in spheres, the latter in yellow needles, and which differs according to its source, whether from plants or the bile of the invertebrata. It appears, then, that entero-chlorophyll is built up in the organ containing it, and that there is a more intimate union between its constituents than in plant-chlorophyll.

V. H. V.

**Bases derived from Pyrroline.** By G. CIAMICIAN and P. MAGNAGHI (*Ber.*, **18**, 2079—2085).—It has been shown (*Abstr.*, 1883, 1442, and this vol., p. 809) that pyrroline and methylpyrroline when treated with zinc and acetic acid, yield hydropyrroline and hydromethylpyrroline respectively. If these compounds are heated



with amorphous phosphorus and hydriodic acid in sealed tubes at  $240-250^{\circ}$ , still more highly hydrogenised compounds are formed.

*Pyrrolidine* (*tetrahydropyrroline*),  $C_4NH_9$ , is obtained with other products from hypopyrroline in the above reaction; it shows great similarity in properties to piperidine, hence the name given to it. It is a colourless, strongly alkaline liquid, boils at  $82-83^{\circ}$ , and has a penetrating ammoniacal odour recalling that of piperidine. It gives an aurochloride crystallising in yellow needles, and unites with methyl iodide, forming methylpyrrolidine.

*Methylpyrrolidine*,  $C_4NH_8Me$ , prepared from hydromethylpyrroline, is a colourless liquid boiling at  $81-83^{\circ}$ , and giving an aurochloride crystallising in yellow plates.

*Dimethylpyrrolidine methiodide*,  $C_4NH_8Me_2I$ , is obtained by the action of methyl iodide on methylpyrrolidine, as a deliquescent, white mass, readily soluble in absolute alcohol, from which it crystallises in large, colourless prisms. When distilled with potash, it yields *dimethylpyrrolidine*,  $C_4NH_7Me_2$ . This boils at  $89-92^{\circ}$ , yields an oily unstable aurochloride, and behaves as a tertiary base, uniting with methyl iodide to form *trimethylpyrrolidylammonium iodide*,  $C_4NH_7Me_3I$ , which crystallises in small needles, and when heated with potash, yields trimethylamine and pyrrolylene, an unsaturated hydrocarbon.

*Pyrrolylene*,  $C_4H_6$ , is gaseous, and is probably identical with Henninger's butine (*Ber.*, 6, 70), as it unites with bromine to form a tetrabromide,  $C_4H_6Br_4$ , crystallising in colourless needles, and melting at  $117-118^{\circ}$ .  
A. J. G.

**Hydroxycomazine.** By F. KRIPPENDORFF (*J. pr. Chem.* [2], 32, 153-176).—*Hydroxycomazine*,  $C_{10}H_6N_3 \cdot OH$  (?  $C_5NH_3 : N \cdot C_5NH_2 \cdot OH$ ), is obtained, together with ammonium carbonate and other products, by the dry distillation of ammonium comenamate. It crystallises in long, colourless, four-sided prisms, melts between  $340^{\circ}$  and  $360^{\circ}$ , and sublimes in similar crystals, with partial decomposition, at a higher temperature. It is nearly insoluble in water, ether, benzene, and carbon bisulphide, soluble in alcohol, and very readily soluble in acids, towards which it behaves as a diacid base. The acid solutions show a green to azure-blue fluorescence. It also dissolves in alkalis to blue fluorescent solutions. It has rather marked toxic properties. The *hydrochloride*,  $C_{10}H_7N_3O \cdot 2HCl$ , crystallises in yellow, six-sided prisms, and melts at  $265^{\circ}$ ; the *platinochloride* crystallises in hair-like, yellow needles. The sulphate, nitrate, hydriodide, aurochloride, &c., are described. The silver-derivative,  $C_{10}H_6N_3 \cdot OAg$ , crystallises in microscopic, short prisms.

Hydroxycomazine is not decomposed by heating with hydrochloric acid, hydriodic acid, nitric acid, nitrous acid, or, either in aqueous or alcoholic solution, by sodium amalgam. Boiling alcoholic or aqueous potash has no action; fusion with potash decomposes it with formation of gaseous products. No definite products, except ammonia, were obtained on distillation with zinc-dust. When reduced by heating with tin and hydrochloric acid, it yields ammonia, piperidine, and amidohydroxypyridine hydrochloride.

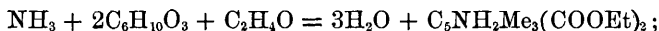
*Amidohydroxypyridine*,  $NH_2 \cdot C_5NH_3 \cdot OH + H_2O$ , crystallises in large

rhombic pyramids, is insoluble in ether, benzene, and chloroform, readily soluble in water and alcohol; it melts at  $214^{\circ}$ , and sublimes in dendritic needles on further heating. It gives a red coloration with ferric chloride. It is a strong base, decomposing ammonium salts when heated with them. The hydrochloride,  $C_6H_5N_2O \cdot HCl$ , platinumchloride,  $(C_6H_5N_2O)_2 \cdot H_2PtCl_6$ , sulphate, nitrate, aurochloride, and other salts are described. When oxidised with nitric acid, it yields oxalic acid.

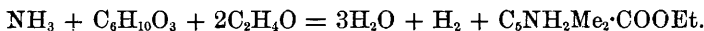
*Comazinic acid* is obtained by the oxidation of hydroxycomazine with potassium permanganate; neither the acid nor any of its salts have yet been obtained in crystals, nor in a state sufficiently pure for analysis.

A. J. G.

**Syntheses of Pyridine-derivatives from Ethyl Acetoacetate Aldehydes and Ammonia.** By R. MICHAEL (*Ber.*, **18**, 2020—2029).—It has long been known that by the action of ammonia (1 mol.) on ethyl acetoacetate (2 mols.) and an aldehyde, pyridine-derivatives are obtained according to the equation (for acetaldehyde)—



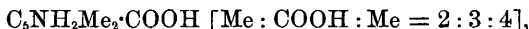
the hydro-compound first formed being converted into a true pyridine-derivative by loss of two atoms of hydrogen. It seemed probable that by increasing the proportion of the aldehyde present, a true pyridine-derivative might be directly obtained according to the equation  $NH_3 + C_6H_{10}O_3 + 3C_2H_4O = 4H_2O + C_5NMe_2 \cdot COOEt$ , but it was found that although a true pyridine-derivative was formed, yet the reaction took a rather different course, leading to the formation, not of ethyl parvolinecarboxylate, but of lutidinecarboxylate:—



The hydrogen is not evolved as such, but yields reduction products.

*Ethyl  $\alpha$ - $\gamma$ -lutidine- $\beta$ -carboxylate* is obtained, in accordance with the above equation, on mixing equal molecular proportions of ethyl acetoacetate, aldehyde-ammonia, and acetaldehyde, the reaction being completed by long heating at  $100^{\circ}$ ; it may be purified by treatment with steam, extraction with ether, and fractionation. The yield is about 25 per cent. of the theoretical. It forms a nearly colourless oil of faint odour, boils at  $246$ — $247^{\circ}$ , and does not distil with steam. It dissolves in mineral acids, but does not form crystalline compounds with them; alkalis reprecipitate it from these solutions. It unites with methyl iodide at ordinary temperatures. It yields a brownish-yellow, crystalline platinumchloride,  $(C_6NH_2Me_2 \cdot COOEt)_2 \cdot H_2PtCl_6$ , melting at  $191^{\circ}$ .

*$\alpha$ - $\gamma$ -Lutidine- $\beta$ -carboxylic acid,*



cannot be prepared directly from its salts; it is therefore best obtained by saponifying the ethyl salt with alcoholic potash, evaporating to dryness, evaporating the aqueous solution with hydrochloric acid, and separating the hydrochloride from the potassium chloride by treatment with absolute alcohol; an aqueous solution of the hydrochloride

is then treated with silver oxide, and the silver chloride filtered off. The free acid crystallises in transparent prisms containing 2 mols.  $\text{H}_2\text{O}$ . It is more soluble in water and alcohol than collidine-carboxylic acid, and yields metallic salts which crystallise badly and are not well characterised. The hydrochloride,  $\text{C}_8\text{H}_9\text{NO}_2\cdot\text{HCl}$ , forms large prisms or thick tables, and melts at  $166^\circ$ ; the platinochloride,  $(\text{C}_8\text{H}_9\text{NO}_2)_2\cdot\text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$ , forms reddish-yellow prisms, and melts at  $216^\circ$ .

When distilled with lime, the calcium salt yields 2:4 lutidine, and the free acid when oxidised yields carbocinchomeric acid,  $\text{C}_8\text{NH}_2\text{COOH}_3$  [= 2 : 3 : 4], from which by heating at  $180^\circ$ , cinchomeric acid was obtained. The supposition that the carboxyl-group of the acetoacetate assumes the  $\beta$ -position relatively to the carboxyl-group is thus confirmed. Experiments with other aldehydes are in progress.

A. J. G.

**Derivatives of Methylhydroquinoline.** By A. FEER and W. KÖNIGS (*Ber.*, **18**, 2388—2393).—*Nitrosokairoline* (nitrosomethylhydroquinoline),  $\text{C}_9\text{NH}_2\text{Me}\cdot\text{NO}$ , is obtained by dissolving kairoline in very dilute sulphuric acid, and adding potassium nitrite to the well-cooled mixture. It crystallises in green plates, does not show a sharp melting point, is readily soluble in alcohol, ether, and benzene, sparingly in light petroleum, and does not give Liebermann's reaction.

*Nitrokairoline*,  $\text{C}_9\text{NH}_2\text{Me}\cdot\text{NO}_2$ , is prepared by adding the calculated amount of potassium nitrate to a solution of kairoline in concentrated sulphuric acid at  $0^\circ$ . It crystallises in long, red needles, melts at  $93$ – $94^\circ$ , and resembles kairoline in its basic properties. *Dinitrokairoline*,  $\text{C}_9\text{NH}_2\text{Me}(\text{NO}_2)_2$ , obtained by treating an acetic acid solution of kairoline with fuming nitric acid, crystallises in golden-yellow plates, melts at  $148^\circ$ , is readily soluble in benzene and chloroform, soluble in alcohol, insoluble in light petroleum.

*Amidokairoline*,  $\text{C}_9\text{NH}_2\text{Me}\cdot\text{NH}_2$ , prepared by the reduction of the nitro-compound with stannous chloride, is a yellow oil; when exposed to air, it acquires a violet-black colour. The hydrochloride and hydrobromide are both deliquescent; the hydrogen tartrate and platinochloride,  $\text{C}_{10}\text{H}_{14}\text{N}_2\cdot\text{H}_2\text{PtCl}_6$ , crystallise well and are sparingly soluble.

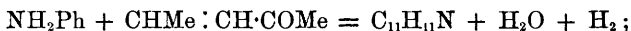
A substance of the formula  $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}$  is obtained by the action of nitrous acid on kairoline. It crystallises with 5 mols.  $\text{H}_2\text{O}$  in fiery-red needles, melts at  $144^\circ$  with decomposition, is readily soluble in alcohol and warm water, and has basic properties. Its solutions in dilute acids show an intense red colour, and are not decomposed on boiling. The hydrochloride,  $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}\cdot\text{HCl}$ , crystallises in red needles. The constitution of this substance is still uncertain, but from its reactions it seems more closely allied to the azo- than to the diazo-compounds.

*Dimethylhydroquinolinium hydroxide* is prepared by heating tetrahydroquinoline with methyl iodide, and decomposing the iodide with excess of alkali. When heated, it is decomposed into kairoline and methyl alcohol.

A. J. G.

**$\alpha$ - $\gamma$ -Dimethylquinoline and the Synthesis of Quinolepidine.**

By C. BEYER (*J. pr. Chem.* [2], **32**, 125—128).—The homologue of quinoline obtained by the author (this vol., p. 672) by the action of hydrochloric acid on aniline, nitrobenzene, and acetone is probably formed by the preliminary condensation of the acetone into the compound  $\text{CMe}_2\text{Cl}\cdot\text{CH}_2\cdot\text{COMe}$ , which is then decomposed into a methyl ketone of crotonic acid, from which, by the action of aniline, the quinoline base is produced according to the equation—



it boils at  $264^\circ$  (uncorr.). The author considers the base to contain a dimethylated pyridine nucleus, the methyls being in the 2': 4' positions.

Quinolepidine identical with that obtained by Wiedel, Hoogewerf, and v. Dorp may be obtained by heating a mixture of paraformaldehyde and acetone, saturated with hydrogen chloride, with a solution of aniline in concentrated hydrochloric acid. The reaction is probably explained by the formation of methyl vinyl ketone by the paraformaldehyde and acetone, which then, by the action of aniline, yields the base according to the equation  $\text{CH}_2:\text{CH}\cdot\text{COMe} + \text{NH}_2\text{Ph} = \text{C}_{10}\text{H}_9\text{N} + \text{H}_2\text{O} + \text{H}_2$ .  
A. P.

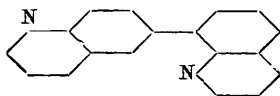
**Action of Acetone on Aniline.** By C. ENGLER and P. RIEHM (*Ber.*, **18**, 2245—2249).—The quinoline base  $\text{C}_{11}\text{H}_{11}\text{N}$  (this vol., p. 672) may be prepared by heating 1 part of aniline with 2 parts of acetone in sealed tubes at  $180^\circ$  for about three days; the free base is set at liberty by the addition of soda, and is obtained in the fraction boiling between  $250^\circ$  and  $280^\circ$ . It forms a yellowish, mobile, refractive liquid, having a quinoline-like odour, and boils at  $263$ — $265^\circ$  (uncorr.). The *chromate*,  $(\text{C}_{11}\text{H}_{11}\text{N})_2\cdot\text{H}_2\text{Cr}_2\text{O}_7$ , crystallises in long, slender, orange-yellow needles. The *sulphate*,  $\text{C}_{11}\text{H}_{11}\text{N}\cdot\text{H}_2\text{SO}_4$ , crystallises in groups of needles; it melts with partial decomposition at  $225$ — $228^\circ$ . The *hydrochloride*,  $\text{C}_{11}\text{H}_{11}\text{N}\cdot\text{HCl}$ , forms slender, flat, needles, and sublimes unaltered.

The authors consider that the acetone is first converted into mesityl oxide, and that it is by the action of aniline on this compound that the quinoline-compound is produced; the base may, in fact, be produced directly by heating mesityl oxide and aniline in sealed tubes at  $130^\circ$ .  
A. P.

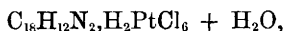
**Trimethylquinoline.** By W. PFITZINGER (*J. pr. Chem.* [2], **32**, 240).—A *trimethylquinoline*,  $\text{C}_{13}\text{H}_{13}\text{N}$ , termed by the author *toluquinoline*, is obtained by the action of hydrochloric acid on a mixture of acetone, paraldehyde, and paratoluidine. It melts at  $63^\circ$ , and boils at  $277$ — $278^\circ$  (uncorr.). The hydrochloride crystallises in yellow needles, and melts at  $260^\circ$ ; the platinochloride,  $(\text{C}_{13}\text{H}_{13}\text{N})_2\cdot\text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$ , crystallises in yellow needles; the picrate and chromate are also described.  
A. J. G.

**Diquinolines.** By O. W. FISCHER (*Monatsh. Chem.*, **6**, 546—555).—In a previous communication (this vol., p. 399), the author described

the preparation of a diquinoline from benzidine by means of Skraup's reaction (Abstr., 1881, 288 and 920). On applying this reaction to diphenylene hydrochloride, a new diquinoline,  $C_{18}H_{12}N_2$ , is obtained. The pure base is deposited from alcohol in colourless plates melting at  $148^\circ$ . It is slightly soluble in water and ether. The constitution of the compound is represented by the formula



The *hydrochloride*,  $C_{18}H_{12}N_2 \cdot 2HCl$ , crystallises in slender needles. The *sulphate* forms white plates. Both these salts are freely soluble in water, but insoluble in alcohol. The *platinochloride*,



is almost insoluble in hot water and hot hydrochloric acid. The *picrate* crystallises in long needles of a yellow colour. It is very sparingly soluble in hot water and hot alcohol. It melts with decomposition at  $268^\circ$ . The chromate forms orange-coloured crystals, which are almost insoluble in water, but dissolve in dilute acids. The *methiodide*,  $C_{18}H_{12}N_2 \cdot MeI$ , crystallises in pale-yellow, silky needles, insoluble in absolute alcohol. The compound softens at  $83^\circ$  and melts at  $126^\circ$ .

Diquinoline forms a tetrabromo-additive product,  $C_{18}H_{12}N_2Br_4$ , and a dibromo-substitution product,  $C_{18}H_{10}Br_2N_2$ . The latter compound does not melt at  $280^\circ$  if perfectly pure.

*Diquinolinesulphonic acid*,  $C_{18}H_{10}N_2(SO_3H)_2$ , crystallises in four-sided plates. The barium salt crystallises in needles with 3 mols.  $H_2O$ . The salt is soluble in water, but insoluble in alcohol.

W. C. W.

**Action of Ethylic Para- and Ortho-nitrobenzoylacetate on Phenylhydrazine.** By L. KNORR and F. JÖDICKE (*Ber.*, 18, 2256—2263).—These compounds are nitro-derivatives of those previously described by Knorr and Blank (this vol., p. 556).

*Ethylic paranitrodiphenylmethylpyrazenecarboxylate*,



is prepared by heating molecular weights of ethylic para-nitrobenzoyl-acetoacetate and phenylhydrazine in acetic acid solution for several hours at  $100^\circ$ . It forms yellowish crystals, melts at  $128^\circ$ , and when treated with excess of concentrated sulphuric acid, yields the *free acid*,  $C_{17}H_{13}N_3O_4$ , a white, crystalline substance which melts at  $202^\circ$ , is readily soluble in alkalis, concentrated acids, and ether, chloroform, &c.; when heated above its melting point, carbonic anhydride is given off, and *para-nitrodiphenylmethylpyrazene*,  $NO_2 \cdot C_6H_4 \cdot C_3N_2HMePh$ , is formed; this distils unaltered under reduced pressure, forming a thick yellowish oil; it is a weak base, its salts being decomposed by water. The *platinochloride*,  $(C_{16}H_{13}N_3O_2)_2 \cdot H_2PtCl_6$ , crystallises in slender needles. By reduction with sodium and boiling alcohol, a base is obtained which dissolves in concentrated sulphuric acid with a deep

crimson colour, becoming more intense on the addition of a trace of nitrous acid.

*Paramidodiphenylmethylpyrazenecarboxylic acid*,



is prepared by the reduction of the nitro-acid with stannous chloride; it is white, crystalline, melts at  $251^\circ$ , and is soluble in alkalis, acids, alcohol, &c., but is insoluble in water; when heated above its melting point, carbonic anhydride is given off, and a heavy oil is formed, which probably is paramidodiphenylmethylpyrazene.

*Ethyllic orthonitrodiphenylmethylpyrazenecarboxylate*,  $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_4$ , is obtained by the action of ethyllic orthonitrobenzoylacetoacetate on phenylhydrazine; it forms yellow crystals, and melts at  $146^\circ$ . Its method of formation and general properties are very similar to those of the para-compound. When heated for some hours with concentrated sulphuric acid at  $100^\circ$ , the *free acid*,  $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_4$ , is formed; this melts at  $218^\circ$ , is monobasic, and is readily soluble in alkalis, concentrated acids, alcohol, &c.; its salts are readily prepared, the ammonium salt is decomposed by long boiling, the free acid being again obtained. When the acid is heated above its melting point for some time, carbonic anhydride is given off, and *orthonitrodiphenylmethylpyrazine*,  $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_2$ , is formed; this may be distilled at  $285^\circ$  under 70 mm. pressure, and crystallises in iridescent scales, which melt at  $95^\circ$ ; by remaining for some time in contact with dilute alcohol, the scales are transformed into slender needles or sometimes into thick prisms, which melt at  $105^\circ$ ; it is a weak base, and shows the pyrazene colour reaction with sulphuric acid, &c.; its salts are decomposed by water. The *platinochloride*,  $(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_2)_2\text{H}_2\text{PtCl}$ , forms thick, orange-red crystals, and melts at  $198^\circ$ . The acid, when reduced with stannous chloride, yields *orthamidodiphenylmethylpyrazenecarboxylic anhydride*,  $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}$ ; but when reduced in presence of free alkali, the alkaline salt of the acid is formed; on acidulating, however, the anhydride is precipitated; it forms slender needles, insoluble in water, alkalis, and dilute acids, but it dissolves in alcohol, ether, &c., and also in concentrated acids, from which it is precipitated unaltered by dilution; it melts at  $261^\circ$ . It is a very stable compound, and by cautious heating may be distilled unaltered; by reduction with sodium and alcohol, it is converted into a compound, which dissolves in concentrated sulphuric acid with a deep green coloration. A. P.

**Cinchona Alkaloids.** By W. J. COMSTOCK and W. KÖNIGS (*Ber.*, 18, 2379—2387; compare *Abstr.*, 1880, 673; 1882, 224; 1884, 1382, this vol., p. 910).—*Methylapocinchene*,  $\text{C}_{18}\text{H}_{16}\text{N} \cdot \text{OMe}$ , is obtained by heating apocinchene with methyl iodide, methyl alcohol, and potash in a reflux apparatus for 10 hours, and extracting the product with ether after distilling off the methyl alcohol; the ethereal solution is washed with water and with soda, and treated with solid potash, when, after a time, yellow needles of the potassium-derivative of apocinchene separate. This is purified by conversion into the sulphate or hydrochloride, treatment with animal charcoal, &c. The free base is an oil

readily soluble in alcohol, ether, acetone, chloroform, benzene, light petroleum, and ethyl acetate, nearly insoluble in water. The *hydrochloride*,  $C_{18}H_{16}N \cdot OMe, HCl + \frac{1}{2}H_2O$ , is obtained in light-yellow crystals melting at about  $198^\circ$ .

*Ethylapocinchene*,  $C_{18}H_{16}N \cdot OEt$ , is prepared in a manner similar to the methyl compound; it crystallises in colourless prisms and melts at  $70-71^\circ$ . When heated at  $130-140^\circ$  with hydrochloric acid, it yields ethyl chloride and apocinchene. If apocinchene is heated with ethyl iodide and ethyl alcohol without the addition of potash, ethyl apocinchene is not formed, the product being apocinchene hydriodide and a crystalline substance, probably apocinchene ethiodide.

*Methylapocinchenic acid*,  $C_{19}H_{17}NO_3$ , is prepared by boiling methyl apocinchene sulphate with dilute nitric acid; it forms colourless crystals, melts at  $233-234^\circ$ , is sparingly soluble in water, readily in alcohol and in alkalis and acids.

*Ethylapocinchenic acid*,  $C_{20}H_{19}NO_3$ , crystallises in anhydrous, yellowish needles, melting at  $161-162$ , or in crystals containing 1 mol.  $H_2O$ , and melting at  $124-126^\circ$ . It is sparingly soluble in water, readily in alcohol, and unites with both acids and bases. When heated with concentrated hydrochloric acid at  $130^\circ$ , it yields carbonic anhydride, ethyl chloride, and a substance melting at  $187^\circ$  and resembling apocinchene in chemical behaviour.

Experiments made to replace the oxygen in apocinchene by chlorine or amido-groups were unsuccessful. Apocinchene only suffers slight decomposition when heated with zinc-dust.

The authors consider that these and their earlier investigations show that apocinchene and cinchonine must contain a second benzene-group in addition to the quinoline-group; the oxygen in apocinchene would seem to be attached to this second benzene-group in the form of hydroxyl, as the compound exhibits decidedly phenolic characters. It is the hydroxylic hydrogen which is replaced in methyl- and ethyl-apocinchene; the reactions of these substances quite exclude the assumption that the alcohol radicles are in union with nitrogen.

A. J. G.

**Artificial Cocaïne.** By W. MERCK (*Ber.*, 18, 2264—2266).—Cocaïne may be prepared by heating benzoylecgonine (this vol., p. 997) with a slight excess of methyl iodide and an equal volume of methyl alcohol in a sealed tube at  $100^\circ$ .

A. P.

**Benzoylecgonine and its Conversion into Cocaïne.** By Z. H. SKRAUP (*Monatsh. Chem.*, 6, 556—562).—The author confirms Merck's observation (this vol., p. 997) as to the occurrence of benzoylecgonine as a bye-product in the preparation of cocaïne. The base crystallises in transparent prisms of the composition  $C_{16}H_{19}NO_4 + 4H_2O$ . When quickly heated, it melts at  $90-92^\circ$ ; sometimes it does not melt below  $120^\circ$  or  $140^\circ$ . The substance which melted at  $90^\circ$  generally resolidifies as the temperature rises, and melts again at  $192^\circ$ . The acetate and sulphate crystallise in prisms. The aurochloride,  $C_{16}H_{19}NO_4 \cdot HAuCl_4$ , forms small, yellow, anhydrous scales, which are soluble in alcohol and sparingly soluble in water. The base is decom-

posed by the action of hydrochloric acid in sealed tubes at 100°, yielding methyl chloride, benzoic acid, and ecgonine.

Benzoylcegonine is converted into cocaine by the action of methyl iodide. W. C. W.

**Alkyl-derivatives of Pilocarpine.** By CHASTAING (*Compt. rend.*, **101**, 507—508).—*Pilocarpine ethiodide*,  $C_{11}H_{16}N_2O_2, EtI$ , is obtained by boiling pilocarpine with ethyl iodide. The excess of ethyl iodide is distilled off, the residue dissolved in absolute alcohol, and the solution concentrated by evaporation until the iodide crystallises out. The crude product is dissolved in water, filtered from the excess of iodine which separates out, agitated with chloroform, and the aqueous solution then evaporated to dryness at a low temperature with as little exposure to light and air as possible. The residue is dissolved in absolute alcohol and the product allowed to crystallise. Pilocarpine ethiodide forms small colourless hygroscopic crystals which melt at about 30°, and are insoluble in chloroform, but dissolve readily in water and in alcohol. The aqueous solution is not affected by hydrochloric acid, nor by a small quantity of ordinary nitric acid, but the fuming acid produces an immediate separation of iodine.

*Pilocarpine ethobromide* is prepared and purified in a similar manner. It is, however, very hygroscopic, and crystallises with difficulty even when carefully dried.

Isoamyl-derivatives are not so easily obtained as the ethyl-derivatives.

*Moniodopilocarpine ethiodide* is formed by the action of ethyl iodide on moniodopilocarpine, or by the prolonged action of an alcoholic solution of iodine on crude pilocarpine ethiodide. It forms white, inodorous crystals, which become yellow when exposed to air and light. It is soluble in water, but insoluble in ether and chloroform.

Attempts to obtain dialkyl-derivatives by the prolonged action of ethyl chloride, bromide, or iodide, were unsuccessful. C. H. B.

**Caffeine Chloriodide.** By E. OSTERMAYER (*Ber.*, **18**, 2298—2299).—Dittmar has recently suggested that only alkaloids containing one or more pyridine-groups give the characteristic clear yellow precipitate with iodine chloride and the reaction with ammonia. The author shows this view to be erroneous, as caffeine, a base which is known not to contain a pyridine-group, readily gives these reactions. *Caffeine chloriodide hydrochloride* crystallises in golden-yellow needles, melts at 175°, and does not decompose when exposed to air. It loses iodine when boiled with water and gives the usual greenish-black precipitate with ammonia. A. J. G.

**Alkaloid in Koch's Cultivating Fluids.** By A. G. POUCHET (*Compt. rend.*, **101**, 510—511).—The liquids employed to obtain pure cultivations of Koch's microbe contain traces of an alkaloid which seems to be identical with that already isolated from the ejecta of cholera patients (this vol., p. 576). If this observation is confirmed by further investigation, it will afford indirect proof that Koch's microbe is really the pathogenic agent in cholera. C. H. B.



**Parahæmoglobin.** By B. LACHOWICZ and M. NENCKI (*Ber.*, **18**, 2126—2131; comp. this vol., p. 825).—When parahæmoglobin is shaken in a closed flask with absolute alcohol saturated with ammonia, a small part dissolves, and the liquid acquires a fine red colour. When this solution is quickly evaporated, a part of the parahæmoglobin separates as a heavy, crystalline powder. If the solution is kept for months, it becomes bluish, and is found to contain hæmatin and albumin. Experiments showed that moisture as well as oxygen is necessary to bring about this change. These results do not agree with those obtained by Struve, who found that glacial acetic acid, sulphuric acid, or chlorine-water, extract the colouring matter from parahæmoglobin without otherwise altering the crystals. The authors were also unable to confirm the results obtained by v. Stein, who prepared colourless crystals of hæmoglobin by treating blood with animal charcoal.

Carbonic oxide hæmoglobin and metahæmoglobin can be kept in alcohol for months without change; in the dry state they become amorphous. N. H. M.

**Chromatology of the Actiniæ.** By C. A. MACMUNN (*Proc. Roy. Soc.*, **38**, 85—87).—Various species of *Actiniæ* contain a colouring matter convertible into hæmochromogen and hæmatoporphyrin; the author proposes to call it *Actiniohæmatin*. It is not identical with actiniochrome, as its absorption-spectrum band occurs nearer the violet; moreover, it occurs in the ectoderm and endoderm, and is respiratory, whilst actiniochrome is confined generally to the tentacles, and is not respiratory.

In the mesoderm of the *Actiniæ*, a green pigment occurs, probably identical with biliverdin, while *Anthea*, *Bunodes*, and *Sagartia* yield a colouring matter resembling chlorofucin, derived from the so-called yellow cells, abundantly present in the tentacles. V. H. V.

**Composition of the Cartilage of Certain Invertebrates.** By W. D. HALLIBURTON (*Proc. Roy. Soc.*, **38**, 75—76).—The cartilage of the *Sepia* and *Limulus* is a chondrin-like substance, giving the reactions of mucin and gelatin; but there is also present a small proportion of chitin. This latter substance exists in the liver of the king crab, but it is uncertain whether it is contained only in the connective tissue or in the liver cells themselves. These results show that chitin is not a substance exclusively epiblastic, but that in the three above-mentioned instances it occurs in mesoblastic structures.

V. H. V.

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## Physiological Chemistry.

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**Calorimetric Investigations.** By M. RUBNER (*Zeit. Biol.*, **21**, 250—254, and 337—410).—The application of calorimetric methods to physiological problems.

**Studies on Peptonisation: Chemical Theory of Digestion.** By T. CHANDELON (*Ber.*, **18**, 1999—2011).—In a previous research the author has shown that hydrogen peroxide converts albumin into peptones (Abstr., 1884, 1390). From this fact, the author deduces two hypotheses: (1.) That the digestive action of pepsin is due to its first producing hydrogen peroxide, which then acts on the albumin and converts it into peptones. Numerous experiments are described, the results of which negative this assumption. (2.) The chemical constitution of pepsin is analogous to that of hydrogen peroxide—as hydrogen peroxide has the formula  $\text{H—O—O—H}$ , so pepsin has the formula  $\text{Pn—O—O—Pn}$  or  $\text{Pn—O—O—H}$ . The author quotes experiments showing the seeming necessity of oxygen for the action of digestive ferments; especially some showing that pepsin, rendered inactive by treatment with sodium carbonate, regains its activity under the influence of hydrogen peroxide. He also shows that when fibrin is gradually added to a pepsin solution until peptonisation no longer occurs, the pepsin is completely precipitated in the form of a compound which is insoluble in glycerol, but is resolved by dilute acids into pepsin and peptones. The author then gives a chemical theory of digestion founded on the second assumption, the evidence for which is by no means conclusive.

A. J. G.

**Digestibility of Varieties of Cheese.** By KLENZE (*Bied. Centr.*, 1885, 564—568).—Of the 18 varieties experimented with, Cheddar was digested in the shortest time (4 hours), whilst unripe skim Swiss cheese required 10 hours for solution; there is no difference in the digestibility of all sorts of hard cheese, or all soft cheese, but all fat cheeses are dissolved the most rapidly, because being open by reason of the fat, they are the more readily attacked by the solvent. There is no connection between the digestibility and the percentage of water present in the cheese, but there is some connection with the percentage of fat and the degree of ripeness. From examination of the quantity of nitrogen dissolved, the author concludes that, on account of its great digestibility, cheese is the most nourishing of all food, meat and eggs excepted.

E. W. P.

**Feeding Sheep with Sugar.** By W. HENNEBERG (*Bied. Centr.*, 1885, 540—545).—The results were similar to those obtained by Märcker and Zimmermann (this vol., p. 1149), but they were somewhat more satisfactory.

E. W. P.

**Earth-nut Cake-meal compared with Rye-meal as Food for Milch Cows.** By F. MEYER (*Bied. Centr.*, 1885, 537—538).—Earth-

nut cake-meal is an advantageous food for milch cows, increasing the yield of milk; whereas the opposite occurs when rye-meal is given.

E. W. P.

**Fibrin Ferment in Blood.** By L. C. WOOLDRIDGE (*Proc. Roy. Soc.*, **38**, 69—72 and 260—261).—As a continuation of the author's investigations on the presence of a substance in blood plasma, which gives rise to the fibrin ferment (compare this vol., p. 571), it is here shown that clear blood plasma, freed from corpuscular elements, deposits on cooling a flocculent precipitate which gives rise to the fibrin ferment. So long as this substance is present, the plasma is coagulable with carbonic anhydride. These phenomena are best observed with peptonised plasma. The above-mentioned precipitate consists of a number of minute round bodies, which collect together into granular masses; these, on standing, cannot be distinguished from ordinary fibrin. Further, this substance exerts the same influence in inducing coagulation as the leucocytes, thus proving that the latter break down to make a part of the proteid constituents of the plasma.

V. H. V.

**Composition of the Milk of the Porpoise.** By T. PURDIE (*Chem. News*, **52**, 170).—The sample investigated was yellow in colour, of a thick consistency, and had a fishy odour. Its sp. gr. differed but slightly from that of water. Its composition was approximately:—Water, 41.11; fat, 45.80; albuminoids, 11.19; milk-sugar (?), 1.33; ash, 0.57 per cent.

D. A. L.

**Essential Nature of the Colouring of Phytophagous Larvæ and their Pupæ.** By E. B. POULTON (*Proc. Roy. Soc.*, **38**, 269—316).

**Action of Antiseptics on Higher Organisms.** By MAIRET, PILATTE, and COMBEMALE (*Compt. rend.*, **101**, 514—516).—The experiments were made under the same conditions as those previously described, the substances administered being iodine and silver nitrate.

The iodine was previously dissolved in alcohol, glycerol and water, or in an aqueous solution of potassium iodide. The results were the same in all three cases. The total quantity of iodine injected varied between 0.21 and 1.92 gram, or between 0.03 and 0.1464 gram per kilo. of body weight. The maximum non-fatal dose is 0.045 gram per kilo., but with more than 0.03 gram per kilo. recovery is very slow. With a larger dose than 0.045 gram per kilo. the animal dies more or less rapidly.

Silver nitrate was injected in aqueous solution in doses varying between 0.036 and 0.074 gram, or between 0.002 and 0.004 gram per kilo. of body weight. With a dose of 0.002 gram per kilo. the animal quickly recovers, but when the amount reaches 0.0028 gram, death invariably follows rapidly.

A detailed account of the symptoms in both cases is given in the original paper.

C. H. B.

## Chemistry of Vegetable Physiology and Agriculture.

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**Glycogen in Ferments.** By L. ERRERA (*Bied. Centr.*, 1885, 549—550).—Starch and glycogen are widely distributed in vegetable organisms: the one in plants, the other in the ferments, but there are a few cases when the appearance is exceptional, namely, of the first in the leaves of *Strelitzia* and *Musa*, of the other in *Claudopus variabilis*; also in a few cases they are totally absent, as in *Monotropa hypopitys* and *Scleroderma vulgare*. The ordinary plants draw their carbon from the air, whilst the ferments obtain it from the soil or substratum. Starch is stored in the cells of the parenchym, whilst glycogen is found in the cells of the pseudo-parenchym, but both only appear in the growing cells, and disappear when growth is complete; from this it is evident that both these substances afford the necessary material for the production of the cells. Most seeds and spores contain oil, which in the one case is converted into starch, in the other into glycogen. Starch is absent from thick-walled cells, but is found in their neighbourhood; and glycogen is absent from paraphyts and completed crystals, and is to be found close to thin-walled elements. Woody and leathery species are poor in glycogen, which is found in 39 out of 46 Basidiomycetes. Those plants and ferments poor in starch and glycogen are, however, rich in oil.

E. W. P.

**Bitter Principle of the Cowberry (*Vaccinium Vitis-Idæa*).** By E. CLAASSEN (*Chem. News*, 52, 78).—The bitter principle of the cowberry is shown to be identical with arbutin. The author points out that as arbutin is decomposed by boiling with most acids even when they are much diluted, all acid should be neutralised before boiling when preparing it from bearberries, otherwise some of the glucoside will be lost.

D. A. L.

**Analysis of the Leaves of *Ilex Cassine*.** By F. P. VENABLE (*Chem. News*, 52, 172).—This shrub, the Yopon, belongs to the same genus as the *Ilex paraguayensis*, and the decoction of its leaves is also used as a beverage, and is very sudorific. The leaves have the following composition:—Water in air-dried sample, 13·19; extracted by water, 26·55; tannin, 7·39; caffeine, 0·27; nitrogen (on combustion), 0·73; ash, 5·75. The ash on analysis yielded the following results:—

CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	MnO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	SO <sub>3</sub> .	Cl.	P <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .
10·99	16·59	0·47	27·02	1·73	0·26	2·50	0·66	3·34	1·32

D. A. L.

**Analysis of *Hyacinthus Orientalis*.** By A. TSCHIRCH (*Bied. Centr.*, 1885, 551).—A fully grown sample of *Hyacinthus orientalis* contains—

Water.....	89.89 per cent.
Dry matter.....	10.11 „
Containing N.....	2.063 „
Ash.....	8.5787 „

Of the constituents of the ash, 46.97 consists of  $K_2O$ , soluble in water, and 16.94  $Cl$ , 6.59  $Na_2O$ , whilst  $MgO$  is present to the extent of 7.219, insoluble in water; the ratio of insoluble to soluble ash is 1:4.76. Comparing this ash with that of *H. non scriptus*, we find more soda present in the last, namely, 16.41, together with  $CaO$  10.35, and  $Cl$  19.99.

E. W. P.

**Caffetannic Acid, Citric Acid, and Quercitrin in Virginia Creeper (*Cissus Quinquifolia*).** By T. L. PHIPSON (*Chem. News*, 52, 65—66).—The extract obtained by soaking the leaves of this plant in water is strongly acid, and citric, caffetannic, and small quantities of tartaric acid have been detected in it. If the extract is saturated with sodium carbonate, and evaporated to a syrup, sodium viridate is formed. When the extracted leaves are treated with dilute soda a large proportion of quercitrin is dissolved before any chlorophyll is taken up.

D. A. L.

**Mineral Matter in the Seeds of Forest Trees.** By R. HORNBERGER (*Bied. Centr.*, 1885, 552—554).

	Ash per cent.	$K_2O$ .	$Na_2O$ .	$CaO$ .	$MgO$ .	$Fe_2O_3$ .	$Mn_2O_4$ .	$P_2O_5$ .	$SO_3$ .	$SiO_2$ .
Elm.....	9.302	32.29	0.62	23.73	6.27	3.24	0.32	11.22	4.86	13.94
Ash.....	4.248	44.18	0.85	21.77	6.57	0.89	0.09	15.21	9.06	1.29
Hornbeam.	2.493	25.15	0.92	35.62	7.82	5.69	2.64	14.28	3.93	5.05
Maple....	6.792	37.37	0.84	27.66	5.82	2.94	2.49	14.16	5.27	6.18
Birch....	4.207	27.03	1.38	23.77	9.20	8.91	2.73	10.89	4.80	8.94
Pine.....	4.288	24.02	0.72	1.63	14.22	2.10	2.05	35.77	4.45	16.00
Larch....	2.076	34.68	1.25	2.41	12.81	1.30	1.83	34.15	4.09	5.88

Generally speaking, the seed contains less lime but more phosphoric acid, magnesia, and potash than the rest of the tree.

E. W. P.

**Ensilage.** By Sir J. B. LAWES (*Agricultural Gazette*, 1885, 2, 13, 93, 117).—These papers contain the results of the feeding experiments with the ensilage whose manufacture and composition were fully detailed in former numbers (this vol., p. 1088). Two sets of feeding experiments were made—one with a number of fattening bullocks, and the other with milch cows. The results of the latter experiment will be described first, since a description of its method and scope and of the rations given has already appeared in the previous Abstract. Very elaborate tables giving the weekly weights of milk yielded by each of the 40 cows during the whole course of the experiments and for the three previous weeks, and also the exact quantities of food given each week, &c., are contained in the original

papers, but the broad results can alone be given here. The principle of the first set of experiments was to feed half the cows on weighed rations of oilcake, bran, hay and straw chaff, and mangels; and with the other half to try the effect of replacing the 80 or 90 lbs. of mangels given daily, by 50 lbs. of red clover silage, estimated to contain an equal quantity of dry food. This programme was adhered to as nearly as the nature of the experiment allowed, with the following results:—Over the whole experimental period of 13 weeks the average yield of milk of the cows receiving clover silage was 25 lbs. 12 ozs. per day, against 27 lbs. 5 oz. yielded by the cows receiving mangels. This corresponds with a difference over the whole period of 14 gallons per head, or of 281 gallons in the lot of 20 cows, in favour of those receiving mangels. The cows fed on the clover silage drank an average of  $1\frac{3}{4}$  gallons more water per head per day than those fed on the more succulent mangels. On the other hand, all the silage-fed cows who remained to the end of the experiment had increased in weight, whilst the mangel-fed cows had on the average lost weight. At the close of the 13 weeks (March 14, 1885), the experiment was varied by the gradual substitution of meadow-grass silage for clover silage—the rations of the mangel-fed cows remaining the same. For the first week  $\frac{1}{4}$  grass silage and  $\frac{3}{4}$  clover silage was given; then half and half for a week; and for the next four weeks grass silage only. One effect of this change was that some of the food supplied to the silage-fed cows remained unconsumed; so that at first less chaff had to be given, then less silage, and, finally, a little mangel had to be given instead of some of the chaff and silage to all of the cows in this lot. The grass silage, it will be noted, contained a larger percentage of dry matter, and especially of woody fibre, than the clover silage. During the six weeks of the experiment, the grass silage-fed cows gave an average of 2 lbs. instead of  $3\frac{3}{4}$  lbs. less milk per head per day than the mangel-fed cows, and they fell off in yield towards the end of the experiment less than the mangel-fed cows. The silage-fed cows in this experiment *lost* weight on the average, whilst the mangel-fed cows *gained* weight. Probably the improved relative yield of milk in the grass silage-fed cows was obtained at the expense of the live weight stored up during the previous experimental ration of clover silage. Regular analyses of the milk were made during the course of these experiments, and from the results it appears that the milk of the mangel-fed cows contained on an average 12·27 per cent. of the total solids, of which 3·45 was butter fat; the milk of the silage-fed cows contained 11·93 per cent. of total solids, of which 3·24 was butter fat.

As regards the experiment with fattening oxen, ten of these animals were carefully selected, and on the 19th of December weighed and divided into two lots—as nearly alike as possible in every respect. One lot of five was to receive 65 lbs. clover silage per head per day; and the other lot 12 lbs. of clover-hay and 50 lbs. of swedes, estimated to contain together as much dry food as the 65 lbs. clover silage. In addition to this, both lots received 6 lbs. oil-cake and  $4\frac{1}{2}$  lbs. barley-meal per head per day. The experiment lasted 16 weeks and 2 days, and the beasts were weighed at the beginning and end, and at two intermediate periods. The total quantity of dry substance consumed

by each lot was, on an average, 24—25 lbs. per head per day, and the quantity of contained nitrogen was practically the same in the two cases.

Taking the result for the whole period—whether we compare the total increase in weight, the average increase per head, the increase per head per week, or per 1000 lbs. live weight per week—there is a very close agreement between the two lots; the one receiving clover silage, and the other very nearly the same quantity of dry substance in clover-hay, chaff, and swedes. The silage has slightly the advantage, but the difference is not more than might be expected in two lots of oxen fed on precisely the same food. Both lots did remarkably well, the silage-fed oxen giving an average increase of rather more, the others of rather less than  $1\frac{1}{2}$  per cent. of their live weight per week.

Sir John Lawes makes the following remarks on the difference in the cropping of the farm necessary to produce clover silage, or, as an alternative, clover-hay and swedes, in the proportions given in the above experiments. A fairly good crop of red clover, cut twice, would weigh about 10 tons per acre in the green fresh state; and, according to the results with No. 1 silo, this would yield only  $7\frac{1}{2}$  tons of clover silage; so that it would require  $8\frac{3}{4}$  acres to produce the 65 tons of silage. The 10 tons of first and second crop green clover would make about  $2\frac{1}{2}$  tons of clover-hay; so that it would require  $4\frac{1}{4}$  acres to produce the 12 tons of clover-hay. There would remain 4 acres for the production of the 50 tons of swedes.

J. M. H. M.

**Report to the Chemical Department of the Highland and Agricultural Society.** By A. P. AITKEN (*Trans. H. and A. Soc.*, 1885, 17, 397—424).—The following analyses of ensilage are given:—

	1.	2.	3.	4.	5.
Water .....	63·10	80·90	76·70	67·60	73·85
Solids .....	36·90	19·10	23·30	32·40	26·15
	100·00	100·00	100·00	100·00	100·00
Solids (dried at 100° C.)					
Albuminoïds .....	3·96	5·18	5·66	4·42	7·03
Non-albuminoid nitrogenous matter .....	1·22	3·50	3·70	4·45	2·81
Sugar .....	3·82	3·24	2·74	1·12	0·96
Other soluble carbohydrates .....	38·24	27·21	36·65	51·77	45·79
Ether extract .....	4·50	14·43	9·18	1·94	5·34
Woody fibre .....	38·04	36·35	32·38	27·97	28·05
Ash .....	10·22	10·09	9·69	8·33	10·02
	100·00	100·00	100·00	100·00	100·00
Acidity reckoned as acetic acid...	0·48	1·25	1·06	0·12	1·37

	6.	7.	8.	9.	10.
Water .....	75·61	73·10	82·15	Hay	Hay
Solids .....	24·39	26·90	17·85		
	100·00	100·00	100·00	—	
Solids (dried at 100° C.)					
Albuminoïds .....	8·62	5·69	10·75	3·45	3·29
Non-albuminoïd nitrogenous matter .....	2·02	2·87	2·18	2·23	0·44
Sugar .....	0·49	2·05	5·72	2·77	2·54
Other soluble carbohydrates .....	47·79	41·55	35·31	41·28	33·54
Ether extract .....	4·89	7·14	5·77	0·57	6·04
Woody fibre .....	26·49	32·60	31·03	38·56	46·01
Ash .....	9·70	8·10	9·24	11·14	8·14
	100·00	100·00	100·00	100·00	100·00
Acidity reckoned as acetic acid ...	1·97	—	0·84	—	—

No. 1. Grasses. Slightly fermented; colour light-brown; odour pleasant.

No. 2. Cocksfoot and meadow fescue, plantain, and white clover; wet, dark-green, and sour.

No. 3. Rough meadow-grass, sweet vernal, and Yorkshire fog, &c.; pale-brown, pleasant odour.

No. 4. Yorkshire fog, bent grass, plantain and other weeds; fruity odour, not acid.

No. 5. Red clover, rye-grass, Yorkshire fog, and wheat-straw; sweet smelling.

No. 6. Oats and vetches; sour, but not unpleasant smell.

No. 7. Rye-grass and clover; sweet vernal, wood-rush, and a few other weeds.

No. 8. Red clover and Italian rye-grass, cut in bloom, and eventually preserved.

Nos. 9 and 10. Grass from which silages Nos. 1, 2, 3, 4 were made. No. 9 chiefly poor Timothy; No. 10 more bent grass, sweet vernal, clover, and weeds.

The author remarks that the sweetest smelling and best preserved silage is generally made of the poorer grasses and weeds.

*Experimental Bean Crop of 1884.*—Beans were grown in 1884 on the plots devoted to manurial experiments on an ordinary rotation of crops, on land not dunged for 10 years, and each plot of which has received the same manure year after year since the experiments commenced. In the ordinary course, rye-grass and clover would have been the 1884 crop; but as this gave a poor result in the previous rotation, beans were substituted, and an excellent crop was obtained, and some very valuable information elicited as to the effect of certain manures on this crop. There were 40 plots in all; but from the results, which



are tabulated in detail, the following specimens are selected which embody general conclusions drawn from the whole series:—

	Grain per acre.	Straw per acre.
	lbs.	lbs.
Plot 3. <i>Ground coprolites</i> , with sodium nitrate and potash salts.....	2239	1008
„ 4. <i>Dissolved coprolites</i> with sodium nitrate and potash salts.....	2755	1568
„ 11. <i>No phosphates</i> with sodium nitrate and potash salts .....	2636	924
„ 12. Bone ash alone .....	300	1008
„ 16. <i>Dried blood</i> with superphosphate and potash salts.....	2496	1680
„ 17. <i>No nitrogen</i> with superphosphate and potash salts.....	2658	1848
„ 18. <i>Sodium nitrate</i> alone .....	364	554
„ 19. <i>Potassium sulphate</i> with superphosphate and sodium nitrate .....	2648	1680
„ 20. <i>Potassium chloride</i> with superphosphate and sodium nitrate .....	2903	1456
„ 21. <i>No potash</i> with superphosphate and sodium nitrate.....	313	252
„ 22. <i>Potash salts alone</i> .....	1630	588
„ 39. } Unmanured .....	502	294
„ 40. }		
„ 38b. Like No. 3, but 2 cwt. “supersulphate of lime” in addition.....	3276	1344

The soil was a stiff clay. Probably on almost all soils potash salts are the most important constituents of bean manures.

*Experimental Barley Crop of 1883.*—The crops yielded by the several plots were submitted to analysis, and the results are discussed in connection with the yields per plot reported in last year's Transactions. The general conclusions arrived at are:—

Nitrogenous manures are the most essential. The quick acting ones (sodium nitrate and ammonium sulphate) are the best, and are best applied as top dressings, *not later* than three or four weeks after the date of sowing. When the top dressing is put on too late the quality of the grain is lowered and the harvest retarded—although there may be an increase in grain and straw. Nitrogenous manures increase the proportion of albuminoids in the grain. Phosphatic manures are next in importance; but unless employed in a quick acting condition, and in conjunction with nitrogenous manures, they produce little effect on ordinary land. -

J. M. H. M.

**Feeding Value of Various Roots.** By A. MAYER (*Bied. Centr.*, 1885, 538—540).—Of various mangolds grown, the largest crop was produced by Golden Tankard seed, the money value also per hectare of this sort was higher than that of any other sort; in fact nearly double that of Mammoth. As regards the value of the individual

roots, Giant Yellow was found to be the best quality, closely followed by Golden Tankard and Yellow Globe. The values employed were 34 pfennigs for albumin and fat, and  $8\frac{1}{2}$  for sugar, &c. Giant Yellow yielded juice of the highest density,  $10\cdot7^{\circ}$ . E. W. P.

**Evaporation of Water into the Atmosphere.** By MASURE (*Ann. Agronom.*, **11**, 289—308; 345—366).

**Farmyard Manure.** By A. AUDOYNAUD and E. ZACHAREWICZ (*Ann. Agronom.*, **11**, 337—345).—From several new analyses of the authors, compared with the well-known ones of Boussingault, the following conclusions are drawn:—

The excrements of the horse and cow contain, on an average, in 1000 parts:—

		Horse.	Cow.
Urine ....	{ Nitrogen .....	15·21	10·50
	{ $P_2O_5$ .....	traces	traces
	{ Potash .....	9·24	13·60
Solid excrements	{ Nitrogen .....	5·58	4·35
	{ $P_2O_5$ .....	3·50	1·20
	{ Potash .....	1·00	0·42

The quantities excreted per diem are—

	Horse.	Cow.
Nitrogen .....	155·6 grams	212 grams
$P_2O_5$ .....	59·5    "	32·4    "
Potash .....	53·8    "	133·7   "

The diet, unless very exceptional, modifies these figures only slightly. A diet poor in nitrogen diminishes the quantity of urea in the urine, but does not influence the proportion of potash. A diet rich in potash does not sensibly influence the proportion of this alkali in the urine or fæces, the surplus being eliminated by the cutaneous excretion of herbivorous animals. The coat of the horse especially contains large quantities of potash, which are to a great extent removed every time the animal is groomed. J. M. H. M.

### Analytical Chemistry.

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**Photometry.** (*Dingl. polyt. J.*, **257**, 65—70.)—From the Report of the Commission of the German Gas and Water Institute, it appears that stearin or spermaceti candles give the same photometric results as the standard paraffin wax candle hitherto employed (in Germany); the wick of the candle and height of the flame being the same in each case. It is proposed to reduce the length of the standard candle to 15 cm. and the weight to 50 grams—the object being to centralise the wick as much as possible.

Hanchard-Moreau (*Bull. de Rouen*, 1885, 99) recommends the use of stearin candles as the standard unit of light for France. Preece suggests a Swan lamp of certain intensity connected with Bunsen's photometer.

According to Krüss the prisms applied by Hefner-Alteneck to Bunsen's photometer give rise to dispersion; he therefore proposes the use of two reflecting prisms. Hefner-Alteneck, in criticising Krüss' remarks, observes, that although dispersion may occur, the effect would not be sufficient to vitiate the results; moreover, if necessary, the simple prisms might be replaced with advantage by achromatic prisms. D. B.

**Elementary Analysis of Gases by Combustion.** By A. EHRENBURG (*J. pr. Chem.* [2], 32, 234—236).—Mixtures of gases containing oxides of nitrogen, and, therefore, not giving good results on eudiometric analysis, yield satisfactory results as regards the percentage contents of carbon, hydrogen, and nitrogen, if burnt in the usual way for nitrogenous substances. The author figures and describes a gas pipette especially designed for the measurement and transference to the combustion-tube of such gaseous mixtures or substances. A. J. G.

**Estimation of Iodides in Presence of Bromides and Chlorides.** By F. L. TEED (*Chem. News*, 52, 104).—When a solution of silver chloride in potassium chloride is precipitated by the gradual addition of a standard iodide solution, saturated, or nearly so, with potassium chloride, the silver iodide clots well, especially when warmed and shaken, and gives good quantitative results. A moderate quantity of bromide does not apparently interfere, but the chloride cannot be entirely replaced by bromide without impairing the sharpness of the end of the reaction. D. A. L.

**Modification of Kipp's Hydrogen Sulphide Apparatus.** By C. REINHARDT (*Dingl. polyt. J.*, 257, 73).—The improvements give the following advantages: (1.) The apparatus may be charged with iron sulphide without removing the acid. (2.) The spent liquor may be run off without the necessity of disconnecting the apparatus. (3.) The flow of acid being regulated by a glass tap, no acid can enter the apparatus whilst it is out of work. (4.) The excess of gas does not escape into the atmosphere, but is absorbed in a vessel placed above the hydrogen sulphide apparatus. D. B.

**Behaviour of Nitrates in Kjeldahl's Method for the Determination of Nitrogen.** By R. WARINGTON (*Chem. News*, 52, 162—163).—This method, as at present constituted, cannot be used successfully in the presence of nitrogen as nitric acid; for either the ammonia present forms ammonium nitrate, and there is a loss of both ammoniacal and nitric nitrogen, or, on the other hand, in the presence of organic matter, the greater part of the nitric acid is reduced, and thus there is a gain in the ammoniacal and organic nitrogen, with a loss in the nitric nitrogen.

When a mixture of dry ammonium sulphate and potassium nitrate

is heated with concentrated sulphuric acid, there is a loss of ammonia equal to the amount of nitrogen added as nitrate; this loss does not, however, occur if a small quantity of water is included in the mixture, for then the nitric acid volatilises with the steam during the earlier stages of heating. Similar experiments in the presence of organic matter indicate that in absence of water, there is a gain in ammoniacal nitrogen, whilst in presence of water, there is a loss. It is therefore important to expel the nitric nitrogen before proceeding to determine the organic nitrogen; this the author accomplishes by a preliminary heating of the organic substance containing the nitrate, with excess of ferrous sulphate and hydrochloric acid.

Ferrous sulphate and sulphuric acid, both with and without water, were found ineffectual for this purpose. D. A. L.

**Volumetric Estimation of Potassium.** By DUBERNARD (*Ann. Agronom.*, **11**, 326—328).—The following solutions are required:—Solution of sodium platinochloride in a mixture of equal volumes of alcohol and water; the solution should contain 12—15 per cent. of the salt. Solution of silver nitrate, containing 12—15 grams per litre. To titrate these solutions, weigh out 0.500 gram pure potassium nitrate or sulphate, dissolve in 2 or 3 c.c. water in a 100 c.c. flask, acidulate with nitric acid, add 20 c.c. of the sodium platinochloride, and fill to the mark with 95 per cent. alcohol. Filter, boil 50 c.c. of the filtrate for a minute with a pinch of zinc-dust (metallic platinum is precipitated and zinc and sodium chlorides remain in solution), make up to 100 c.c., filter, and titrate 50 c.c. of the filtrate with silver nitrate. The cubic centimetres of silver nitrate employed, multiplied by 4, is the quantity necessary to precipitate the chlorine left in solution in 20 c.c. of sodium platinochloride, after precipitation of 0.500 gram pure potassium nitrate or sulphate. The quantity of silver nitrate necessary to precipitate the chlorine originally present in 20 c.c. of sodium platinochloride, is found by measuring 10 c.c. of the latter into a 100 c.c. flask, boiling with zinc-dust, making up to 100 c.c., filtering, titrating 50 c.c. of filtrate with silver nitrate, and multiplying the cubic centimetres used by 4. The difference between these two quantities of silver nitrate is the quantity corresponding with 0.500 gram pure potassium nitrate or sulphate, and is to be marked on the bottle.

In actual analysis, 5 grams of the substance are brought into solution and made up to 100 c.c.; 10 c.c. of this is taken for the estimation, which is conducted as above described. When chlorides are present in the solution of the sample, another 10 c.c. must be directly titrated with the silver nitrate, and correction made accordingly. No test analyses are cited by the author. J. M. H. M.

**Determination of Soluble Potash in Soils.** By QUANTIN (*Ann. Agronom.*, **11**, 367—374).—The readily assimilable potash in a soil may be considered to be the portion soluble in water plus the portion rendered insoluble by the action of organic matter, but readily set free on the destruction by decay or fermentation of this associated organic matter. When strong acids are employed in the estimation

of available potash, not only are the two amounts of potash above-mentioned brought into solution, but the potash-bearing minerals of the soil are also attacked to some extent, and yield up a larger or smaller quantity of potash, which, under the circumstances of actual cultivation, would be slowly liberated during the lapse of perhaps several years. In order to arrive more truly at the "minimum of available potash," the author uses the following process:—

The sample is incinerated at a low red heat. This is best done as Schloesing recommends, by placing it in a boat heated in a combustion-tube, and passing a current of carbonic anhydride until tarry vapours disappear, then gradually replacing the carbonic anhydride by oxygen, until a current of pure oxygen traverses the tube. If the incineration is properly conducted, the potash originally soluble in water, remains so, and that combined with organic matter becomes soluble on the destruction of the latter. After the incineration, boiling water is used to extract the potash. From the examination of eight soils cited by the author, it appears that the potash obtained in this way is from 0.07 to 0.45 per cent. less than that extracted when strong acids are used.

When acids are to be employed for the purpose of obtaining results comparable with those obtained by the ordinary process, the author recommends the following mode of procedure, which shortens the time necessary by one half, without any sacrifice of accuracy:—

To ascertain the volume occupied by the sample, place the 25 or 50 grams of soil in a flask marked at 50 c.c., and measure, by means of a burette, the volume of water necessary to fill the flask to the mark. Transfer the water and soil to a basin, add nitric acid gradually until effervescence ceases, and evaporate to dryness on a sand-bath, continuing the heat until nitrous fumes cease. The heat should not exceed a dull red. Stir the residue with boiling water for 15 minutes, then add ammonium carbonate solution until the liquid just smells of ammonia. Introduce the contents of the capsule into a litre flask, make up to the mark with water, and shake at intervals for two hours. Throw the whole on a plaited filter, collect 900 c.c. of the filtrate, evaporate to dryness, ignite gently, digest with 50 c.c. dilute hydrochloric acid, concentrate to 20 c.c., and add platinum tetrachloride. The potassium platinochloride thus obtained is very pure. The volume occupied by the insoluble residue is taken to be the same as that of the original sample of soil. Even if this volume were altogether neglected, and the flask assumed to contain 1000 c.c. of water, the authors show that, in assaying 25 grams of soil containing 0.400 per cent. of potash, the error would be only 0.0048 per cent. in excess.

J. M. H. M.

**Estimation of Small Quantities of Sodium Chloride in Crude Potassium Chloride.** By F. RÖTTGER and H. PRECHT (*Ber.*, 18, 2076—2078).—The estimation of very small quantities of sodium chloride in presence of potassium chloride is very difficult. The authors find that good results are obtained by treating the dried chlorides with alcohol of 90 per cent. (by weight). The extract contains all the sodium chloride with a small quantity of potassium

chloride, and separation can be effected by evaporating to dryness, weighing the mixed chlorides so obtained, and then estimating the potassium as platinumchloride in the usual manner. 100 parts of 90 per cent. alcohol at 15° dissolve 0.345 part of sodium chloride and 0.073 part of potassium chloride. Any magnesium chloride present is separated by adding potassium carbonate to the alcoholic solution. A. J. G.

**Detection of Iron, Aluminium, Chromium, Manganese, Cobalt, Nickel, Calcium, and Magnesium (as Phosphate) in the Precipitate Produced by Ammonia.** By C. L. BLOXAM (*Chem. News*, 52, 109—110).—The author proposes a method for the detection of Fe, Al, Cr, Mn, Co, Ni, Ca, &c., in the precipitate produced by ammonium chloride and ammonia, after oxidation, in the filtrate from the separation of the hydrogen sulphide group of the ordinary qualitative course. The precipitate is dissolved in hot dilute hydrochloric acid, and this solution is boiled with excess of potash; the filtrate contains any aluminium phosphate and phosphoric acid. The precipitate is redissolved in hydrochloric acid, and the solution treated successively, first with ammonium acetate, which precipitates iron and chromium phosphates, then with sodium phosphate, and is boiled; the precipitate contains a phosphate, the non-phosphatic iron and chromium of the original precipitate. The filtrate is then treated with excess of ammonia, the calcium, barium, strontium, and magnesium (originally present as phosphate), probably manganese or cobalt, or both, are precipitated, whilst nickel and some cobalt remain in solution. The method has been found to work well. When a solution containing iron, nickel, and cobalt is precipitated with ammonium chloride and ammonia, more cobalt than nickel comes down with the iron, and in fact, cobalt can be roughly separated from nickel by this means. When iron and chromium are to be separated by oxidation with bromine, the chromium phosphate must be previously decomposed with sodium carbonate. Large quantities of chromium may be separated from iron by boiling the mixture with potash and potassium ferricyanide; potassium chromate is formed. D. A. L.

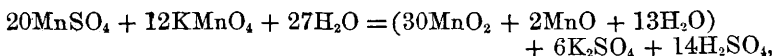
**Estimation of Manganese.** (*Dingl. polyt. J.*, 257, 199—205.) Wolff's volumetric method of estimating manganese in iron and its ores necessitates the presence of the manganese in the form of proto-salt, and the iron in the form of chloride. The ferric oxide is precipitated with zinc oxide, and the manganese titrated with potassium permanganate in presence of the iron precipitate.

According to Reinhardt, the gravimetric estimation of manganese by precipitation with bromine gives satisfactory results. The method may be shortened by dissolving the iron ore in hydrochloric acid of sp. gr. 1.19, oxidising with nitric acid or potassium chlorate, filtering into a litre flask, neutralising the filtrate with ammonium carbonate, precipitating with ammonium acetate (faintly acid) at a boiling heat, cooling and making up with water to 1 litre. The manganese in 300—500 c.c. of the filtrate is then precipitated.

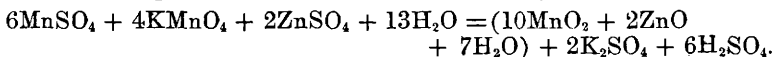
For the determination of manganese, Jüptner adopts the following

method :—The hydrochloric acid solution of the substance to be estimated—in which any ferrous salt must be previously oxidised with potassium chlorate—is neutralised with sodium carbonate in a graduated measure, treated with ammonium chloride, precipitated in the cold with barium carbonate, and, after adding an excess of ammonia, digested for some time with agitation. It is then filled to the mark, well mixed and filtered. A certain measure of this filtrate is treated with sulphuric acid, filtered, neutralised with ammonia, heated to boiling, and precipitated with ammonium sulphide. It is then filtered, and washed with water saturated with ammonium sulphide. If the precipitate is small, it may be treated directly with boiling acetic acid. With larger quantities, the precipitate is washed with acetic acid through the filter into a beaker. The solution is filtered into a tared platinum basin, evaporated to dryness, ignited and weighed as  $Mn_3O_4$ .

According to Meinecke the action of potassium permanganate on a manganoous salt is expressed by the equation—



whilst in the presence of a zinc salt the following reaction occurs :—



According to Volhard, the presence of chlorides interferes with the success of his method; Meinecke, however, finds that the results are not so wanting in accuracy as to warrant the evaporation with sulphuric acid recommended by Volhard. In order to obtain an oxide free from protoxide, a large excess of zinc is required. Meinecke adds from 25 to 30 grams of zinc sulphate to the solution to be titrated. He also recommends the use of an excess of potassium permanganate to ensure the complete oxidation of the manganese. The excess is then titrated back with antimony trichloride.

D. B.

**Separation of Titanium from Aluminium and Iron.** By F. A. GOOCH (*Chem. News*, **52**, 55—57, and 68—70).—By numerous experiments, the author shows that in the presence of free acetic or formic acid, titanium is precipitated from its solutions by alkaline phosphates, ammonia, &c., whilst aluminium is not; and as the present methods of separating titanium from aluminium are all of them unsatisfactory, the author proposes and describes methods founded on the above reactions. In one method, the solution is mixed with sodium ammonium hydrogen phosphate, formic acid, and ammonium formate; in the other method, the solution is treated with acetic acid and sodium acetate, and is then boiled. The precipitates in both cases go through a series of washings, fusions, &c.; the first method is tedious, owing to the inconvenient state of the precipitate, whilst in the second method the numerous simple operations have to be repeated four times before a good separation of the two metals is effected. If iron is present it is removed beforehand by means of hydrogen sulphide, in presence of ammonia and ammonium tartrate.



The hydrogen sulphide is boiled off, and the tartaric acid oxidised by permanganate, then the solution is ready for the above treatment. In treating silicates containing both titanium and phosphoric acid, the residual insoluble silica should be treated with sulphuric and hydrofluoric acids, to recover as insoluble titanitic phosphate any titanium deposited with the silica.

D. A. L.

**Decrease of Dissolved Oxygen in Deep-well Waters, and a Simple Method for taking Samples in Deep Borings.** By B. LEPSIUS (*Ber.*, 18, 2487—2490).—The researches of Finkener and others have shown the desirability of water for domestic purposes having a high percentage of dissolved oxygen. The author has examined samples of water obtained at various depths in the new borings in diluvial and tertiary sandstones at Frankfort. In three samples taken at depths of 12, 13, and 25 metres, the percentages of oxygen to total dissolved gases were 24.06, 21.97, 12.90, respectively. An apparatus is also described for taking samples from small borings, without the water coming into contact with the air or with surface waters.

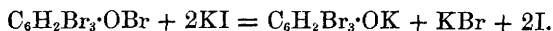
L. T. T.

**Biological Examination of Water.** By C. J. H. WARDEN (*Chem. News*, 52, 52—54, 66—68, 73—76, 89, and 101—104).

**Valuation of Ozokerite.** By B. LACH (*Chem. Zeit.*, 1885, 905, and *Dingl. polyt. J.*, 257, 259).—100 grams of ozokerite are treated with 20 grams of fuming sulphuric acid in a tared basin. The mixture is heated at 170—180°, and stirred until all sulphurous anhydride has been expelled. On re-weighing the basin the difference gives the loss in volatile constituents. 10 grams of residues from the manufacture of potassium ferrocyanide, previously dried at 140°, are then added. A tenth part of the mixture is weighed into a tared filter, and extracted with benzene at 60—80° in an extracting apparatus; The loss represents the yield of wax.

D. B.

**Titration of Phenol with Bromine.** By C. WEINREB and S. BONDI (*Monatsh. Chem.*, 6, 506—510).—Benedikt has pointed out (*Wien. Akad. Ber.*, 1879), that when a solution of phenol is mixed with an excess of bromine-water, tribromophenol bromide is formed, not tribromophenol, as stated by Landolt (*Ber.*, 4, 770). In Koppeschaar's method of estimating phenol (this Journal, 1877, i, 746) an excess of bromine-water is added to the solution of phenol; potassium iodide is added to the mixture, and the amount of iodine liberated is estimated by means of a standard solution of sodium thiosulphate. The tribromophenol bromide is decomposed by the potassium iodide, yielding potassium bromide, iodine, and tribromophenol—



Better results are obtained if a mixture of sodium bromide and bromate is substituted for bromine-water. Although this method yields satisfactory results with pure phenol, it cannot be successfully applied to crude carbolic acid or tar oils, as it is exceedingly difficult

to completely extract the phenol from such oils by shaking with water. If the crude carbolic acid is itself subjected to the action of bromine-water, the bromine only acts on the surface of the oil globules.

W. C. W.

**Determination of the Strength of Vinegar and Acetic Acid.** (*Dingl. polyt. J.*, **257**, 74).—For the rapid estimation of the acidity of vinegar and acetic acid, Hartmann and Hauer's volumetric method is recommended.

D. B.

**Action of Lime on Quinine.** By A. R. HASLAM (*Chem. News*, **52**, 97).—Experimental evidence is adduced to show that quinine is decomposed by heating with lime at low temperatures. One gram of quinine sulphate mixed with lime was found to lose 0.032 gram after exposure to a temperature of 70° for four hours, whilst at 100° the mean loss in five experiments was 5 per cent.

D. A. L.

**Modification of the Nitrometer for Use as a Ureometer and other Purposes.** By G. LUNGE (*Ber.*, **18**, 2030—2032).—A modification of the author's nitrometer, in which by means of the three-way tap the measuring tube can be connected with a small flask in which decompositions such as that of urea by sodium hypobromite, &c., are effected, the volume of gas evolved being then read off in the usual way in the nitrometer.

A. J. G.

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## Technical Chemistry.

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**Preparation of Carbons for Electric Lamps from Furfuraldehyde or Fucusaldehyde.** By A. SMITH (*Dingl. polyt. J.*, **257**, 338).—For the production of carbon filaments for incandescent lamps, hydrogen chloride is passed through furfuraldehyde or fucusaldehyde. A black liquid is obtained which is placed between glass plates. After 8—10 hours, a thin layer of carbon separates, the thickness of which may be regulated by inserting threads or wires of suitable size between the plates. The carbonaceous layer is removed from the plate, cut into strips of the requisite width, twisted and heated to 100°. The filaments thus obtained are then heated to a high temperature in closed crucibles or porcelain tubes, through which a current of marsh-gas is passed. The electric resistance of the filaments may be changed by the addition of  $2\frac{1}{2}$  per cent. of lamp black to the furfuraldehyde or fucusaldehyde, before subjecting them to the above treatment.

For the preparation of carbon rods for arc lamps, lamp-black or finely powdered carbon is mixed with from 60—70 per cent. of furfuraldehyde or fucusaldehyde, and the mixture subjected to powerful pressure in suitable moulds. The rods thus formed are exposed to

the action of gaseous hydrogen chloride, after which they are heated strongly in closed crucibles covered with powdered carbon.

D. B.

**Electric Accumulators.** (*Dingl. polyt. J.*, **257**, 329—335.)

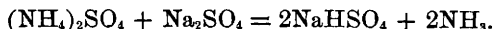
**Filtration of Sewage through Peat.** By A. MÜLLER (*Bied. Centr.*, 1885, 509—511).—Two forms of peat, litter and dust, have been employed; the latter is compact, and permits of only slow filtration, whereas the former must be kept sunk below the liquid. Chlorine, sulphuric, and silicic acids pass through unabsorbed, whilst the more valuable compounds, such as phosphates, are retained; ammonia is not oxidised, as is the case with aerated peat. The total amount of mineral matter in the filtrate is not much lower than that in the sewage, whilst the total solids are increased by much organic matter.

E. W. P.

**Manufacture of Chlorine from Calcium Chloride.** (*Dingl. polyt. J.*, **257**, 259).—An important feature in the production of chlorine from calcium chloride by means of silica and alumina being the maintenance of the temperature required to effect the decomposition, Solvay and Company recommend the addition of broken porcelain or bricks, siliceous or calcareous substances to the charge, which falling down gradually heat the ascending current of air.

D. B.

**Preparation of Ammonia from Ammonium Sulphate.** By E. CAREY and F. HURTER (*Dingl. polyt. J.*, **257**, 253).—To obtain ammonia from ammonium sulphate and simultaneously utilise the sulphuric acid, the authors propose to mix it with 1 equivalent (or more) of sodium sulphate, and heat the mixture at 350—370° in the presence of aqueous vapour. The following reaction occurs:—



The hydrogen sodium sulphate is heated with salt to form hydrochloric acid and sodium sulphate, or it is treated for the production of anhydrous sulphuric acid.

D. B.

**Preparation of Potassium Sulphate.** By H. MÜLLER (*Dingl. polyt. J.*, **257**, 299).—By subjecting a mixture of equal parts of magnesium sulphate, potassium chloride, and ferric oxide to fusion, the author obtains potassium sulphate and a combination of magnesia with ferric oxide. The latter is sparingly soluble in water, and insoluble in a saturated solution of potassium sulphate.

D. B.

**New "Sulphate" Furnace.** By T. LARKIN (*Dingl. polyt. J.*, **257**, 161).—This furnace, worked by the St. Bede's Chemical Company, consists of an ordinary decomposing pan charged through the top, and a newly constructed mechanical roaster. The roaster is a muffle furnace having a flat inner arch, the intervening space being divided into transverse compartments. The furnace is heated by a double series of small fires, one series heating the bed and the other

the arch. Each fire has its own flue leading into a main flue, from which the heat can be directed under the pan. The mechanical appliances for working the charge consist of a vertical shaft with horizontal arms fitted with scrapers. The agitator is worked from below, so that it is protected from the direct action of the fire, a special feature of the furnace. The application of a number of fires easily regulated is also an improvement of the greatest advantage; in fact, the whole furnace is heated evenly, and the temperature maintained regularly, so that expansion and contraction of the brickwork cannot take place. To regulate the temperature with still greater ease each flue has a damper. The flues are so arranged that a slight draught to the chimney suffices. The draught in the interior of the muffle furnace is stronger than that in the flues, so that no gaseous hydrogen chloride can escape through leakage. The fact that all working doors are closed during the evolution of gas is important, inasmuch as the furnace can be worked with a stronger draught than in the case of ordinary furnaces. The condensation of the hydrochloric acid is perfect, acid of high concentration only being obtained.

D. B.

**Improvements in the Soda Industry.** (*Dingl. polyt. J.*, **257**, 110—113.)—Mond and Jarmay have patented a process for removing the ammonium salts present in the sodium bicarbonate obtained by the ammonia soda process. For this purpose the crude salt is dissolved in warm water and the solution allowed to cool, when pure bicarbonate separates, and all the ammonia remains in solution. The operation of cooling the solution may be effected in various ways, and the mother-liquor separated from the crystals by centrifugal machines. When the solution of the crude sodium bicarbonate is effected under pressure in an atmosphere of carbonic anhydride, a higher temperature may be employed; it is necessary, however, to cool the solution down to 65° before running it off. The mother-liquor may be used repeatedly for washing and dissolving fresh crude bicarbonate.

For the purification of sulphuric acid, Thomson recommends the treatment of chamber acid with ammonium sulphide in order to precipitate arsenic and antimony. The acid is then filtered through finely divided lead, and concentrated in the usual manner.

Pechiney and Weldon have found that in preparing chlorine from magnesium oxychloride it is necessary to first heat the salt at a comparatively low temperature in order to expel part of the water, and then to heat the desiccated salt in a current of air or oxygen. About 60 per cent. of the chlorine of the oxychloride is thereby driven off as free chlorine, and the remainder as hydrochloric acid. By neutralising the acid with magnesia, converting the magnesium chloride into oxychloride, and treating the latter as above described, all the chlorine is obtained in a free state.

D. B.

**Preparation of Strontium Carbonate.** By E. A. MEBUS and J. W. DECASTRO (*Dingl. polyt. J.*, **257**, 198).—Finely pulverised strontium sulphate is digested in a solution of ammonium carbonate. The decomposition is effected in apparatus fitted with agitating appliances.

D. B.

**Manufacture of Zinc Oxide.** By F. C. GLASER (*Dingl. polyt. J.*, 257, 113).—Zinc oxide ores or roasted zinc blendes are mixed with a binding medium, and coke or other reducing agent, made into bricks and heated in a reverberatory furnace. The vapours of zinc, on coming into contact with the atmosphere, are converted into zinc oxide, which is collected in condensing chambers. D. B.

**Behaviour of Basic Copper Carbonate with Nascent Hydrogen.** By C. HASSACK (*Dingl. polyt. J.*, 257, 248—253).—In a communication on the cleaning of monuments, Bauer observed that the changes giving rise to the formation of the black film with which most of our monuments are covered, are probably of a reducing character. This statement is confirmed by the invariable presence of organic matter in the black film, which in decomposing acts as a reducing agent. It was shown by experiment that copper carbonate and hydroxide exhibit characteristic changes when exposed to the influence of reducing agents.

The author has investigated this subject experimentally. To study the action of reducing agents, plates consisting of malachite and mixtures of precipitated copper hydroxide and carbonate were employed. The following are the details and results of the experiments:—

	Original malachite. I.	Malachite digested in soda ley. II.	Malachite after exposure to the action of nascent hydrogen.	
			III.	IV.
Cu.....	56·78	65·84	74·43	74·73
O .....	14·47	16·15	16·40	17·51
H <sub>2</sub> O .....	8·78	14·98	6·14	6·04
CO <sub>2</sub> .....	18·52	1·58	1·28	1·02
CaO .....	0·12	0·17	0·25	0·27
Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> ..	0·28	0·28	0·30	0·32
Insoluble ....	0·38	0·35	0·36	0·39

To arrive at the probable constitution of the different substances, the calcium oxide is calculated as carbonate, whilst the remainder of the carbonic anhydride, and the whole of the water, are calculated as being combined with copper (as CuCO<sub>3</sub> and CuO<sub>2</sub>H<sub>2</sub>). Hence the following numbers are obtained:—

	CuCO <sub>3</sub> .	CuO <sub>2</sub> H <sub>2</sub> .	CuO.	Cu <sub>2</sub> O.	CaCO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .	Insoluble.
I.	51·52	47·29	—	—	0·21	0·28	0·33
II.	4·04	80·72	13·96	—	0·30	0·28	0·35
III.	3·02	33·11	39·66	22·25	0·44	0·30	0·36
IV.	1·49	32·55	51·73	13·05	0·48	0·32	0·39

	Original mixture of precipitated copper hydroxide and carbonate.	Treated with soda ley		Exposed to nascent hydrogen		
		3 days.	4 days.	2 days.	3 days.	4 days.
Cu .....	60·84	62·48	63·41	66·51	66·73	68·02
O .....	15·29	15·74	15·98	14·52	12·42	13·62
CO <sub>2</sub> .....	9·78	0·89	0·83	0·88	0·67	1·04
H <sub>2</sub> O .....	13·42	19·34	18·81	15·95	17·96	15·33

The results of these experiments seem to confirm this assumption as to the cause of the blackening of the patina of bronze statues erected in large towns. It appears that the green film formed by the action of carbonic anhydride and water is first contaminated with particles of inorganic and organic matter, and that subsequently and in consequence of the putrefaction of the organic matter, reduction and decomposition occur, accompanied by similar appearances to those obtained in the above experiments. D. B.

**Aluminium Sulphite.** By F. BECKER (*Dingl. polyt. J.*, **257**, 300).—The author has used hydrogen aluminium sulphite for the purification of beet-juice at the Slibowitz Sugar Refinery. It is obtained by dissolving aluminium hydroxide in an excess of sulphurous acid. A solution of 1·167 sp. gr. contains 4·37 per cent. Al<sub>2</sub>O<sub>3</sub> and 13·90 per cent. SO<sub>2</sub>. To obtain a solution of the normal salt, Al<sub>2</sub>(SO<sub>3</sub>)<sub>2</sub>, an excess of aluminium hydroxide is employed. This solution is very unstable. D. B.

**Producing a Coating of Ferrosoferric Oxide on Iron.** By M. HONIGMANN (*Dingl. polyt. J.*, **257**, 211).—The articles to be treated are digested in a boiling solution of caustic soda or potash previously saturated with ferric oxide. D. B.

**Improvements in Metallurgy.** (*Dingl. polyt. J.*, **257**, 235—247.)—According to the *Société des Acières de Louvry* the addition of manganese to iron ores is effected by employing coke prepared with this metal. For this purpose coal and manganese ores are ground together, and the mixture is then carbonised. A saving of one-half the quantity of manganese usually employed is said to be realised.

To dephosphorise or desulphurise pig-iron, Hoepfner uses a furnace with acid or basic lining, loosely packed with broken bricks, rich in limestone or chalk, and mixed with ferric or manganic oxides.

To utilise the heat of the flame of the Bessemer converter, it is proposed by Williamson to combine the Bessemer and the hearth-smelting processes.

For the production of malleable ingot iron and steel, Mathesius recommends the following process. The basic Bessemer process is conducted in the ordinary manner until the commencement of the dephosphorisation, when tar, petroleum, or other reducing agents are

introduced into the metallic bath in conjunction with the blast, the object being to complete the dephosphorisation in an atmosphere, which, owing to the high temperature and the strongly basic character of the slag, is said to act as an oxidiser of the phosphorus and a reducing agent to the remaining metals.

In producing ingot iron by the hearth-smelting process, F. Siemens, of Dresden, recommends the retention of a certain portion of the fused metal in tapping the charge and the rapid introduction of a fresh quantity of pig iron. He claims to effect a saving in (1) loss of metal, (2) destruction of the furnace, (3) time and labour, and (4) heat.

In order to utilise coal-dust for gas regenerative furnaces, McFarlane has constructed the bed of the furnace of a refractory material with perforations through which a mixture of air and steam is passed.

Atwood's process for refining iron involves the use of an amalgam of lead. Its action is not, however, explained.

Bramall has constructed a smelting furnace fitted with four regenerating chambers for heating the air and gases before they enter the furnace. Whilst the gases pass through one pair of regenerators, the flue gases escape by way of the other series. The operation may be reversed by altering the valves and dampers. D. B.

**Chromium Chlorate.** By E. LAUBER and C. WEINREB (*Dingl. polyt. J.*, **257**, 290).—In 1877 Storck and de Conink recommended the use of chromium chlorate in cotton printing, but from a number of causes, especially the cost of production, the application of this compound has been limited. Storck produced his chlorate in the printing colour by mixing chrome-alum with barium chlorate, whereby a large proportion of the latter was consumed in converting the potassium sulphate of the chrome-alum into potassium chlorate—a reaction of no value as regards the conversion of chromium chlorate into chromic acid.

Some time ago one of the authors succeeded in preparing chromium chlorate more cheaply on a large scale, by precipitating a solution of 60 kilos. of chrome-alum in 80 litres of hot water, with 20 kilos. of ammonia soda dissolved in 60 litres of water, well washing the precipitate, and dissolving it in 10 kilos. of cold sulphuric acid of 66° B. After filtration, the solution is treated with 22 kilos. potassium chlorate, dissolved in 50 litres of water. Potassium sulphate crystallises out, the mother-liquor containing chromium chlorate. The chlorate thus obtained is available for use in printing, and gives a good steam catechu or steam chrome-brown, but does not yield a good logwood black. It appears that oxidation alone is insufficient for the fixation of hæmatoxylin, and that the development of the black colour requires the presence of a metallic oxide.

A number of receipts for printing with chromium acetate, as prepared by the authors, is given at the end of the paper. D. B.

**Preparation of Tungstic Acid.** By A. K. HUNTINGTON (*Dingl. polyt. J.*, **257**, 340).—Wolfram, schellite, or other tungsten ores are



fused with carbonated or caustic alkalis and a flux (for instance, quartz). The alkaline tungstate is tapped off, or the slag may be removed, leaving the tungstate. Should the tungstate contain impurities, it may be refined by fusing it again with addition of sodium silicate, glass, or other substance that will take up the impurities and form a slag that can be separated from the tungstate.

The tungstate thus obtained is ready for use, or it may be dissolved in water and crystallised, or treated for the production of tungsten oxide and metallic tungsten. D. B.

**Steeping of Barley.** By C. BERNREUTHER (*Bied. Centr.*, 1885, 363—364).—Barley was steeped under pressure and compared with some steeped under ordinary conditions, the time of steeping being however varied. It appears that the pressure exerts no influence in hastening the process, and moistening with water for various short periods, amounting in all to 24 hours, was as effective as when the grain was immersed for 70 hours. E. W. P.

**The Sorghum Sugar Industry in the United States.** By CAPUS (*Ann. Agronom.*, 11, 308—326).—A *résumé* of two American reports, one by a Committee of the National Academy of Sciences (Washington), and the other by H. W. Wiley, Chemist to the Department of Agriculture, Washington.

Messrs. Weber and Scovell give the detailed composition of the sorghum cane (var. Orange) as follows:—Water, 76.58; glucose, 3.00; cane-sugar, 9.77; starch, 4.12; cellulose, 4.54; oil, 0.07; gum and acids, 0.24; soluble albuminoids, 0.23; insoluble albuminoids, 0.16; soluble ash, 0.68; insoluble ash, 0.06; total, 99.45. The ash contains:—Silica, 27.91; ferric oxide, 0.14;  $P_2O_5$ , 5.37;  $MnO$ , 0.89; lime, 6.82; magnesia, 4.64;  $SO_3$ , 6.23; potash, 46.48; soda, 0.98; sodium chloride, 0.42; total, 99.88. The seed contains:—Sugar, 0.56; starch, 63.09; cellulose, 6.35; water, 12.51; ash, 0.64; albuminoids, 7.35; oil, 3.08; tannin, 5.42 (?); total, 99.00. Amongst the acids found in the plant are malic and aconitic acids.

122 samples of 35 varieties of sorghum cultivated in the latitude of Washington, yielded the following mean results:—

Juice .....	58.57	per cent.
Density of juice .....	1.0813	
Cane-sugar .....	16.18	„
Glucose .....	1.80	„
Soluble organic matters .....	3.08	„
Available sugar, 16.18—(1.80 + 3.08)	11.30	„

The density of the juice varies from 1.040 to 1.080, and each augmentation of 0.001 corresponds with increases of 0.238 per cent. of cane-sugar, 0.028 per cent. of organic matter, 0.262 per cent. of available sugar; and to a diminution of 0.052 per cent. of glucose. The cane-sugar of the sorghum undergoes very ready inversion under certain circumstances, and this fact is a great difficulty of the industry as it stands at present. Should the plant be touched by frost *before maturation*, then as soon as the thaw sets in inversion takes

place. Again, inversion begins to set in almost as soon as the canes are cut, and in the course of two or three weeks very little cane-sugar is left. Some experiments of Wiley's hold out the hope that it may be possible to preserve the canes in silos without loss of sugar. Only 60 per cent. of the maximum quantity of juice is obtained by expression in the mills. On an average of 40 samples,  $87\frac{1}{2}$  per cent. of the cane-sugar originally in the juice remains in the syrup after defecation and concentration. But few experiments have been made on the action of different manures, but such as are recorded appear to show that farmyard manure exercises an influence which, if not actually injurious, is at any rate not beneficial. J. M. H. M.

**Manufacture of Cane-sugar from Starch.** By L. AUBERT and V. GIRAUD (*Dingl. polyt. J.*, **257**, 298).—When starch is treated with water saccharose is formed according to the equation  $2C_6H_{10}O_5 + H_2O = C_{12}H_{22}O_{11}$ . Glucose combines with starch, also producing saccharose, thus:  $C_6H_{10}O_5 + C_6H_{12}O_6 = C_{12}H_{22}O_{11}$ .

To conduct these operations on a large scale 100 kilos. of potatoes are digested at  $100^\circ$  in 1 cubic metre of water containing 5 kilos. of sulphuric acid. An electric current is passed through the starch solution, the electrodes consisting of antimonial lead. The end of the conversion is determined by a solution of iodine, which should give no colour reaction. The current is then interrupted, and the solution treated with calcium carbonate and an excess of calcium hydroxide, to decompose the dextrose and glucose which have escaped the action of the electric current. Before proceeding with the subsequent process of filtration and saturation with carbonic anhydride, basic lead acetate should be added, in order to precipitate the colouring matters. On evaporating the solution to a syrupy consistence, and allowing the mass to crystallise, a product is obtained giving by analysis—

Water.	Ash.	Grape-sugar.	Cane-sugar.
6.95	3.67	1.00	88.38 per cent.

Density = 1.502. Specific rotatory power =  $+68.6^\circ$ . D. B.

**Preparation of Tetrachlorophthalic Acid.** (*Dingl. polyt. J.*, **257**, 300).—According to the *Ges. für chem. Ind. in Basle*, tetrachlorophthalic anhydride is obtained by heating 5 kilos. of phthalic anhydride with 30 kilos. of antimony pentachloride at  $200^\circ$  for some time, and subsequently passing a current of chlorine through the fused mass. After 8 to 12 hours' action, nearly all the phthalic anhydride used is converted into tetrachlorophthalic anhydride, which is separated from the melt by distillation. D. B.

**Saponification of Fats by Electricity.** By ROTONDI (*Dingl. polyt. J.*, **257**, 210).—The author finds that fats may be saponified by means of sodium chloride, by passing an electric current through the solution, and using suitable diaphragms. The products obtained are soap, glycerol, and free chlorine. D. B.

**Treating Vegetable Tallow.** By B. LACH (*Chem. Zeit.*, 1885, 941, and *Dingl. polyt. J.*, 257, 120).—Although the vegetable tallow recently brought into commerce, and consisting of tripalmitin, may be readily saponified with lime under pressure, yet the product is wanting in appearance, and cannot be pressed. By mixing equal parts of bone-fat and vegetable tallow, a more satisfactory product is obtained. D. B.

**Cultivation of the Star Anise Tree and the Preparation of the Oil in Annam.** (*Pharm. J. Trans.* [3], 16, 91—92.)

**New Coal Tar Colouring Matters.** (*Dingl. polyt. J.*, 257, 324—329.)—According to Dahl and Co., the separation of  $\beta$ -naphthylaminemonosulphonic acid is effected in the following manner:—The solution containing the calcium salt obtained from the mixture of the sparingly soluble monosulphonic acids of  $\beta$ -naphthylamine, is evaporated to a pasty consistence, and allowed to remain for two days. It is then filtered and pressed. The residue consists of the mixed calcium salts of the three  $\beta$ -naphthylaminemonosulphonic acids, the acid I predominating, whilst Brönner's acid II is present in considerable quantity. The filtrate after a time yields crystals of the calcium salt of the acid III. It is concentrated by evaporation, and filtered after cooling. From the mother-liquor, which contains  $\beta$ -naphthylaminesulphonic acids and impurities, the former are extracted by treatment with hydrochloric acid. To prevent the formation of impurities, it is proposed to conduct the operation in the following manner:—85 kilos. of  $\beta$ -naphthylamine sulphate are gradually introduced into 270 kilos. of sulphuric acid, 66° B. at 15—20°. The mixture is agitated for some time (48—70 hours). The sulphonic acid III thus formed is converted into the sodium salt, and the latter extracted by means of alcohol. The salt is obtained in a pure form, available for the production of colouring matters.

According to the *Farbwerke, vormals Meister Lucius und Brüning*, the ethyl carboxylates of hydroxyquinaldines and hydroxyquinizines are obtained by the action of ethyl acetonedicarboxylate on amines and hydrazines. On saponification the free carboxylic acids are produced. On heating, carbonic anhydride is evolved, and the acids are resolved into the hydroxyquinaldines and hydroxyquinizines obtained by Knorr by the action of ethyl acetoacetate on amines and hydrazines.

For the production of alkylised pseudoquinols (quinoline-derivatives in which the nitrogen is combined with methyl or ethyl, and the carboxyl-groups occupy the para-position to the nitrogen), the *Farbwerke, vormals Meister Lucius und Brüning* have patented a process depending on the action of ethyl acetoacetate and its substitution products on secondary aromatic amines. According to Ewer and Pick colouring matters varying from yellow to brown are obtained by acting with carbamides on aromatic amines and tetra-alkylised derivatives of diamidobenzophenone. By fusing carbamide with dimethylaniline hydrochloride and anhydrous zinc chloride, a yellow dye is produced. Similar colours may be obtained by the action of cyanic acid, carbamide and their derivatives on aromatic

amines in the presence of condensing agents. For instance, from diphenylcarbamide and ammonium chloride, from carbamide and aniline hydrochloride, from carbanilamide or monophenylcarbamide and aniline hydrochloride, and from carbanil and aniline hydrochloride. D. B.

**Formation of Aniline Black.** By K. ZÜRCHER (*Dingl. polyt. J.*, 257, 162).—From the author's observations, it appears that the slow development of aniline black on the fabric from the usual printing colours at temperatures varying between  $-13^{\circ}$  and  $+13^{\circ}$  is favoured by certain conditions of humidity and of motion of the surrounding atmosphere. At  $25^{\circ}$  the development of aniline black is perfectly normal. D. B.

**Use of Antimony Oxalate in Printing.** By E. JACQUET (*Dingl. polyt. J.*, 257, 168).—Instead of fixing aniline colours mordanted with tannin in a bath of tartar emetic, the author recommends the addition of a mixture of basic antimony oxalate and ammonium oxalate to the printing colour. The basic salt is obtained by precipitating potassium antimonate with ammonia, and is added in the form of paste, together with twice the weight of ammonium oxalate to the printing colour. The goods are then steamed and cleared with the addition of chalk to the bath, in order to neutralise the excess of oxalic acid. D. B.

**Fixation of Alumina as a Discharge on Indigo Blue.** By A. SCHEURER (*Dingl. polyt. J.*, 257, 113).—Some time ago the author showed that certain metallic chlorides and sulphates, when steamed in the presence of potassium dichromate, discharge indigo blue. A mixture of potassium dichromate and aluminium chloride destroys vat blue after steaming for one minute. The printing colour consists of 790 parts of starch thickening, 60 parts of potassium dichromate, and 150 parts of aluminium chloride of  $34^{\circ}$  B. The process is trustworthy, and requires no special precautions. The fabric after passing through the Mather and Platt's steaming machine should have a lemon colour on the printed parts. The products of the reaction are aluminium and chromium chromates, and chromium and aluminium oxides. After steaming, the goods are rinsed, dyed with alizarin, and soaped. The reds obtained in this manner were found to be lacking in brightness, and exhibited a greyish-violet tinge due to the simultaneous fixation of chromium oxide on the fibre.

The author is of opinion that a probable explanation of the inferiority of the red, is the retention of chromium oxide in combination with a product of decomposition of the indigo, better results being obtained by substituting aluminium oxalate for the chloride. In this case, oxalic acid must be added. By comparing the reds produced on an original and a discharged white, each treated with potassium dichromate, aluminium oxalate and oxalic acid, the shades on the former were found to be considerably brighter. These results appear to confirm the above assumption. D. B.

# ERRATA IN VOL. XLIV.

Page	Line	
871	14 from top,	for $C_6H_3BrNO$ read $C_6H_3Br_2NO$ .
"	" " "	" $(C_6H_3Br_2O)_2, H_2PtCl_6$ read $(C_6H_3Br_2NO)_2, H_2PtCl_6$ .

# ERRATA, VOL. XLVIII.

Page	Line	
1	17 from bottom,	for "41, 548," read "41, 549."
245	7 " top,	" "155°" read "185°."
"	9 " "	" "185°" " "191°."
364	19 " "	" "Kiesel" read "Kissel."
516	5 " "	et seq., for "pyrroline" read "pyrroline."
518	4 " bottom	for "metaxylene" read "paraxylene."
530	5 " top	" "mono- and dinitro-anisöl" read "mono- and dinitro-bromanisöl."
603	13 " "	" resin " read "styracin."
"	" "	" styracin " read "resin."
620	" " bottom,	" mangrove" read "mango."
772	12 " "	" 33° " read "330°."
834	18 " top,	" per cent." read "per 1000."
1049	21 " "	" chloride" read "oxalate."
1097	5 " "	" 1884 " read "1885."
1161	19 " "	" iron is dissolved in cupric chloride, steel in hydrochloric acid," read "the iron or steel is dissolved in ammonium- or sodium-cupric chloride."
"	22 " "	after the word "residue" insert "should be well washed with warm dilute hydrochloric acid."
1190	3 " "	for "andesite" read "andesine."
1242	13 " bottom,	for "and also a red fluorescence of the solution," read "Both chlorophylls exhibit a red fluorescence."